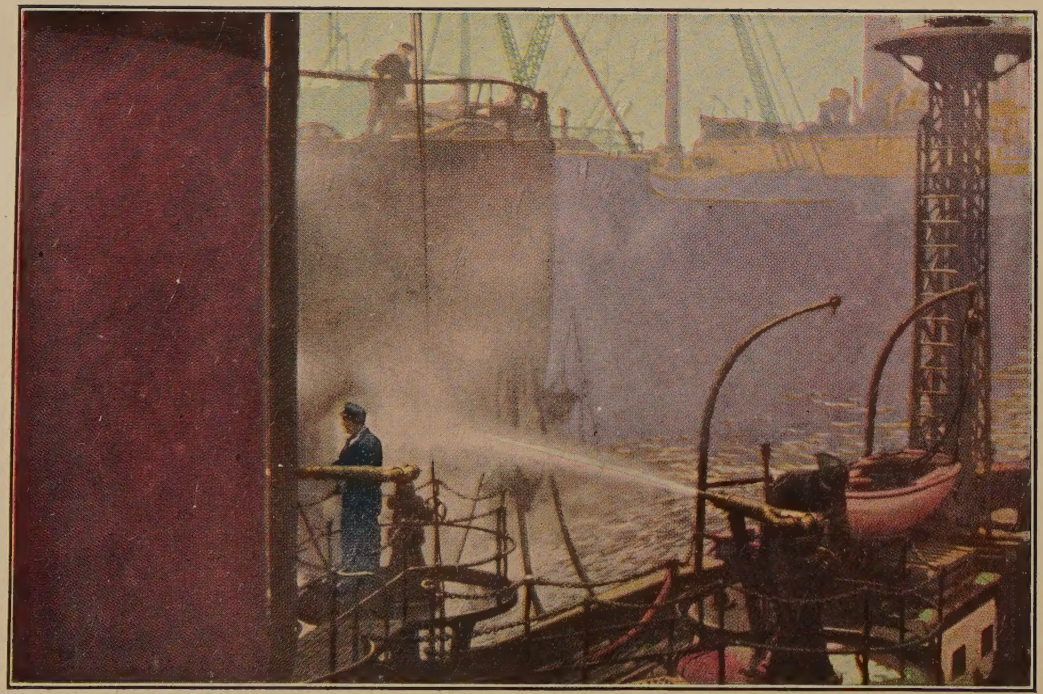

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ASSOCIATED WITH SEVEN VOLUMES
WITH A MEMORIAL SCIENCE, GLOSSARIES
AND A GENERAL INDEX

SUPPLEMENTED BY A LOOSE-LEAF VOLUME EMBODYING
THE MOST IMPORTANT DEVELOPMENTS IN SCIENCE,
ANNUALLY FROM 1923 TO 1932

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VOLUME EIGHT

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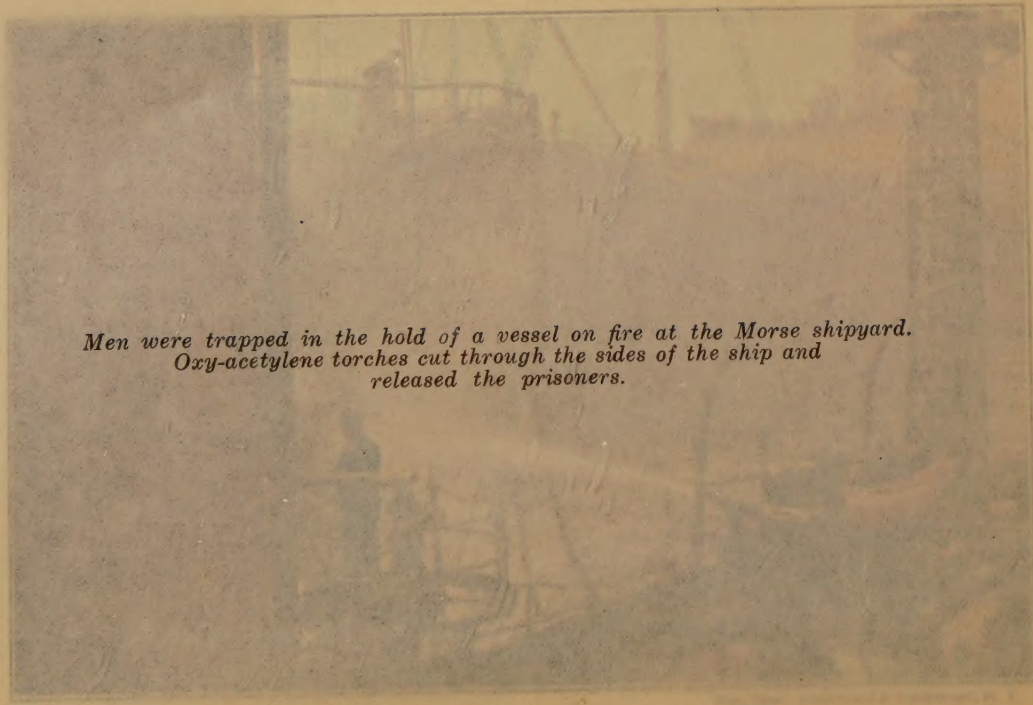

Men were trapped in the hold of a vessel on fire at the Morse shipyard. Oxy-acetylene torches cut through the sides of the ship and released the prisoners.

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CHEMISTRY

The Science of Matter and Its Changes

BY

HIPPOLYTE GRUENER

Professor of Chemistry, Western Reserve University

P. F. COLLIER & SON COMPANY
NEW YORK

PREFACE

THE emphasis throughout this work is upon the fundamental principles underlying the subject. Without this emphasis the reading of the wonders of chemistry may develop into mere pastime. The most important chapter, therefore, is that dealing with general chemistry, the groundwork upon which all the rest is based. There are here interwoven descriptions, general principles and applications, selected with the view of building upon the general knowledge and experience of the reader.

The applications of organic chemistry are receiving increasing attention. These applications are mainly in the direction of food and physiological chemistry and of the organic industries. This increased interest calls for a more thorough grounding in the principles of organic chemistry than has been common in the past. A comprehensive view of this subject has therefore been included.

The technique of analytical chemistry may be acquired only in the laboratory; but enough of this subject is introduced to give the reader some conception of how the nature of substance is determined.

The nature of the chapter on the chemistry of nutrition may be indicated by the subheadings; composition of animal and vegetable matter, the source from which each is built up and the matter and energy cycles involving them; the constituents of foods, carbohydrates, fats, proteins, condiments, mineral matter and water; function of each of these

and their digestion, absorption and utilization; composition of common foods, fuel values and food requirements; vitamines; the chemistry of cooking; food analysis, adulteration and preserving. The subject is treated always from the chemical standpoint.

The chapter on sanitary chemistry deals with the vitiation and purification of water supplies, sewage and garbage disposal, impure air and ventilation and the chemistry of disinfectants.

The discussion of agricultural chemistry may be summarized thus: relation of animal and vegetable life; the composition and the building up of the material of plants; nature of soils, their exhaustion and renewal; the nitrogen question.

Manufacturing processes in which chemical principles are involved are constantly increasing in number. The more important of these are discussed, either in the main text, or in the special chapter devoted to the subject. The extraction and manipulation of metals, the alkali and acid industries, salts, ceramics and the electrochemical process are the most outstanding of these. The organic industries exhibit a growth which is even more striking. Predominant among them are the great petroleum industry; the coal-tar industry, not of such great volume, but branching out into such interesting ramifications as the dyestuffs and the synthetic drugs; the sugars, starch and its alteration products, cellulose; the fermentation industries; textiles, dyeing and bleaching; fats and oils, paints and varnishes; organic explosives; organic electrochemistry; chemical warfare.

The glossary will be found convenient for reference.

HIPPOLYTE GRUENER.

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CHAPTER I

THE NATURE OF CHEMICAL CHANGES

WHEN a chemical action takes place, and a chemical change results, the effect is often apparent to the ordinary observer. But the reasons why this change takes place, and the manner of its taking place are so far from apparent that it presents serious difficulties to the novice in chemistry. Iron rusts, it changes, it ceases to be the strong metallic substance we are used to. It is converted into a brown brittle powder which is only a nuisance. The mechanic has no interest in the rust; for him the iron has been destroyed, he drops all thought of it and looks for new material. For the chemist the matter is different. He must know what is happening, and why: what the iron has changed to, and what is involved in the process. If questions like these are fully answered, the knowledge gained will quickly lead to the appreciation and solution of the next problem, and thus our understanding of chemistry has made a beginning. In all chemical considerations we must follow with care every circumstance. If, like the mechanic, we say that the iron is gone, and the discussion closed, we shut ourselves out from one of the first chemical principles, namely the study of the *change* which has taken place. It is often difficult for the beginner to realize that the change which seemingly destroys the object before him,

does not end the discussion, but is in reality the subject matter of his thought. A serious difficulty met with at the outset of the study of chemistry is that there are rather few common experiences, in any sense clearly appreciated, upon which we can draw for our material for chemical discussions. Chemical happenings of a familiar nature are few in number. The following array includes most of them: combustion, or burning of fuel or other matter; rusting or corrosion of metals; decay and fermentation of animal and vegetable matter; plant growth and food assimilation by animals; explosions; and a more or less vague experience with the corrosive action of chemical substances, as acids and alkalis. And in all men's experiences the attention is usually given to nonchemical phases of the event, with no penetrating thought as to what lies at the foundation of these experiences.

The reason for men's neglect of chemical thoughts lies in part in the fact that the chemical aspect of familiar experiences has apparently no practical features. Further, in the familiar chemical changes, some of the reacting substances and products are gases, and therefore escape observation. But probably the greatest difficulty lies in the nature of the changes. Chemical forces act at small distances, and the unit masses involved are so minute that it is with great difficulty that we can form a mechanical picture or conception of that which is happening. Without some mechanical conception our mental processes are indeed slow. We make progress by applying our past experience to the present problem. Correlating our experience of large readily appreciated masses with the minute masses and distances of chemistry is a matter of

very great difficulty, and the one great stumbling-block in the study of our subject.

Chemistry is often described as the study of the nature of matter and the changes which it undergoes, but a more complete and suggestive description has been given as follows: Chemistry is the study (*a*) of the nature and composition of matter, (*b*) of the changes in its fundamental nature which matter undergoes, (*c*) of the causes of these changes and influences controlling them, (*d*) of the energy changes involved, and (*e*) the laws found to govern them. In order to make this concrete let us take a familiar and important chemical happening, namely combustion, or burning, and, as a special case, the burning of sulphur. We will first describe the action, and then interpret it with the above points in view.

In order to cause sulphur to burn, it must be lighted, that is, heated sufficiently to start the burning. As it burns, the sulphur unites with the active constituent of the air, oxygen, and in doing so develops enough heat to give what is called a blaze. The sulphur disappears, and we know that a limited supply of oxygen is soon exhausted, and in place of these two a new substance appears, a gas with a well known pungent odor. This gas is made up of both sulphur and oxygen, and its weight is the same as the combined weight of the two. Its name, sulphur dioxide, indicates its composition.

In this simple process much of what is stated above is illustrated. (*a*) First as to the composition of matter. We can see that the oxide of sulphur, which results from the burning of the sulphur, is made up of simpler parts, namely oxygen and sulphur, and is therefore a complex substance, called a compound. It will develop presently that by no

known process can it be shown that sulphur and oxygen are complex. They seem to be simple substances, incapable of resolution into any constituents. These then are "elements," and may be considered the fundamentals of chemistry. (*b*) In the process of the union of sulphur and oxygen, which we call burning, we see a characteristic change: its opposite is the separation, called decomposition, of a complex into its simpler parts. (*c*) We say that sulphur and oxygen exhibit affinities for each other, and under the influence of the heat applied, when the sulphur was set on fire, the affinity asserted itself so that they combined. (*d*) In the burning heat is developed. This means that energy is being liberated. In chemical changes we are concerned with energy in the form of chemical energy, heat, light, electricity, and mechanical energy. They are all intimately related. Chemical energy and heat are the forms which will receive most of our attention.

In order to familiarize ourselves somewhat more fully with some phases of the subject let us consider the combustion of charcoal and of gasoline. Chemically the material of charcoal is called carbon, and it is the same as that of ordinary coal and of soot. It is an element, like sulphur and oxygen. Ordinarily carbon does not alter in the air, and we say that its affinity under ordinary conditions is slight, otherwise it would at all times unite with the oxygen of the air. But when carbon is heated sufficiently it burns, that is, unites with the oxygen, for that is what the process of burning or combustion is. The charcoal and oxygen concerned both gradually diminish, and in their place is a colorless, odorless gas, carbon dioxide, so inconspicuous that it needs special tests for detecting it. But in the use of

stoves and furnaces, the escape of this gas must be provided for, and is one of the functions of the chimney. The burning of gasoline is more complicated, for gasoline is made up of two elements, carbon and hydrogen. The presence of the former is evident in many ways; the hydrogen is less evident without further study. Both of these elements, carbon and hydrogen, have affinity for oxygen when heated, hence their combination burns readily. This burning means that each element present unites with oxygen much as it would were it by itself. Each forms its own oxide. Carbon forms carbon dioxide, mentioned above, and hydrogen forms water, which is made up of hydrogen and oxygen. This is indicated by its formula, H_2O.

These points are made a bit more graphic if they are represented by a simple form of symbolism, called the chemical equation.

1. For sulphur burning, $S + 2\,O \rightarrow SO_2$, sulphur dioxide.
2. For carbon burning, $C + 2\,O \rightarrow CO_2$, carbon dioxide.
3. For gasoline burning, $CH_2 + 3\,O \rightarrow CO_2 + H_2O$.

Another familiar chemical experience is the corrosion of metals. Some metals, particularly iron, have affinity for oxygen, even at ordinary temperatures, but more so when heated. Hence they corrode, that is, become covered with a layer of oxide, which is a combination of the metal with oxygen. Silver will not tarnish with oxygen, but does unite with sulphur which is occasionally present in the air. If we wish to understand these changes better we may again use equations.

$2\,Fe + 3\,O \rightarrow Fe_2O_3$, iron oxide.
$Cu + O \rightarrow CuO$, copper oxide.
$2\,Ag + S \rightarrow Ag_2S$, silver sulphide.

When we study chemical changes, and form chemical compounds, we are often confronted with these questions. Have we really performed a chemical change, or is it merely a physical change, which has taken place? And when two substances are put together, have they really combined, or have they only formed a mixture? After some progress has been made in this study, such questions cause little confusion. At the beginning, however, the distinction must be carefully drawn, and methods applied for determining the nature of the change.

Physical changes come under the titles of mechanics, heat, light, sound, electricity and magnetism. It will be noticed that these are all concerned with the energy changes of a body, rather than with the nature of the substance of that body. A piece of iron is in motion or comes to rest. Its energy is important, but the body is always the same iron. When heated the platinum wire glows, or water is converted to steam, but upon cooling the change will be seen to have left the matter unaltered. Light may traverse a transparent medium, or be reflected by a bright surface, but it makes no impression on the nature of the matter. A wire will vibrate and give out sound, or be conducting electricity, but later will be seen to be absolutely unaltered. The following statement covering such cases is crude perhaps, but will serve as a very usable formula. A physical change is one of such nature that when the influences bringing about the change are removed, the substance involved reverts to its original form. In a chemical change the substance is permanently altered. For example, when the sulphur was heated in the air it was permanently converted into a sub-

stance, sulphur dioxide, of an altogether different nature.

The case of the difference between a mixture and a compound may be shown by the usual laboratory illustration of iron and sulphur. If we mix iron filings and sulphur powder and examine the product, we will notice, if we use care enough, that the iron is still present as iron, and the sulphur as sulphur. A magnet attracts the iron and leaves the sulphur; while, if the mixture is shaken up with water, the heavier iron may be separated. If we now heat a mixture of sulphur and iron the mass is seen to glow and all individual characteristics of the sulphur and iron are gone. We may formulate as follows: In a mixture the different constituents preserve their individuality and may be separated by proper mechanical means; in a compound the constituent elements have lost their individuality and have become merged into a new substance with its own set of characteristics.

It will be convenient to state three canons by which we may decide whether a chemical change has taken place. They are: (*a*) in a chemical change heat is usually developed or absorbed; (*b*) after the change the substances involved show different characteristics; (*c*) in chemical changes the proportions of reacting substances involved are always definite. If there is an excess of one constituent it simply remains behind like so much inert matter.

CHAPTER II

NATURE AND CONDUCT OF MATTER

IF we make a survey of substances which come under our observation, including those of a less common nature, found only in certain industries and chemical laboratories, we may notice that they fall into two classes, one of simple substances, the other of their compounds. The simple substances, or elements, include the metals, and a number of nommetallic substances, as carbon, sulphur, and oxygen. No process has ever served to simplify them; nothing can be substracted from them; they can be changed only by adding to them. It is evident that the other class, that of the compounds, includes substances which may be further divided, which in fact are made up of two or more elements. Elements unite to form compounds, as the sulphur and oxygen united to form sulphur dioxide, and compounds can be resolved into their constituent elements. These ideas are fundamental and our nomenclature is based upon them. The name silver sulphide is thus interpreted at once, and we may at a glance receive considerable information from it.

The element, being the simplest form of matter, may be used as the basis for the study of our subject. About ninety such individual substances, or elements, have been identified, and each is a starting point for a whole set of compounds. But in spite of the vast array of individuals which such a

fact suggests, the whole subject is simplified by the very ready grouping of all the elements and their compounds, so that they may be comprehended within comparatively few divisions. The elements fall into two classes, the metals and the nonmetals. The exact chemical characteristics of the metals must be left for later study, but the usual impression of what constitutes a metal is correct as far as it goes. Malleability, high specific gravity, opacity, and conductivity for heat and electricity, are the most outstanding features of metals. These are all physical properties, but the chemical properties which characterize metals belong to substances possessing these physical properties. The common metals conforming to these conditions are zinc, aluminium, manganese, chromium, iron, cobalt, nickel, tin, lead, copper, arsenic, antimony, mercury, silver, gold, and platinum. From a chemical standpoint, however, the list is not complete and another group of metals must be added, the common members of which are sodium, potassium, calcium, and magnesium. These metals conform to the usual ideas of metals in most respects, but they are not heavy and possess such high chemical affinities that they cannot be used for ordinary purposes.

The second class of elements consists of the nonmetals. The name is a weak one, as is also the description that these elements do not possess the properties of metals. It is nevertheless convenient. The physical properties of nonmetals are varied, but when we come to their chemical properties we find that they stand out strongly as a group. The nonmetals are these:

Oxygen, a gas, the active constituent of the atmosphere. Easily the most important element.

Hydrogen, a light gas which burns with great readiness. It unites with oxygen to form water.

Carbon, the element making up the major portion of charcoal, coal, graphite, and the diamond. Carbon is the fundamental element of living organisms.

Nitrogen, a gas, the inert constituent of the atmosphere. In compounds of vital importance in the animal and vegetable world.

Although these four elements are rather dissimilar, there are advantages in grouping them together. They serve as good illustrations for studying chemical reactions, for their reactions are typical, and come within the range of ordinary human experience, so that we may illustrate from them freely. These four elements are sometimes called the "organogens," because they are the main elements which go to make up organic matter. Organic matter is of somewhat complicated composition, so that its study requires special attention. This branch of chemistry is studied under the name of "Organic Chemistry."

Fluorine, chlorine, bromine, and iodine form a group of elements so similar that they must be considered together. Their names are not unfamiliar, but iodine is the only one likely to be familiar as an element. Chlorine is a constituent of common salt, and is the most important of the group. They are called halogens, meaning salt formers, because they are constituents of typical salts.

Sulphur is a common element and it is well known that it occurs in combination, as in coal and some mineral waters.

Phosphorus is associated with matches. It is exceedingly inflammable, hence dangerous as well

as useful. It is a constituent, as may be surmised, of the minerals called phosphates.

Boron is found in borax and boracic acid.

Silicon is the fundamental element of the mineral world. Its compounds are not active under ordinary conditions, hence they interest the chemist less than they do the mineralogist. The former wishes to experiment in his own laboratory. But he can perform only in a small way the great reactions which have taken place in the mineral world, which involve vast periods of time, masses, pressures and temperatures, all on a scale which he finds it impossible to repeat.

As was stated above, all terrestrial matter is made up of elements, and theoretically can be resolved into these and built up from them. But many of these elements are rare and the great bulk of the earth's crust is made up of a small proportion of them. Eight elements, oxygen, silicon, aluminium, iron, calcium, magnesium, sodium, and potassium, make up more than 97 per cent, ten more make up over 2 per cent, and all the rest are comprehended within the narrow range of one-half per cent. One must be careful not to obtain false impressions from these relative values. Sulphur, for example, makes up only one-tenth per cent of the earth's crust, yet the absolute amount is considerable, and where conditions have been favorable for its concentration, it is found in abundance. Most of the common metals, also, are present in relatively small amounts, yet like sulphur, seem abundant when concentrated.

The classification of the elements into metals and nonmetals is a fundamental one, dominating the whole range of chemical study. The idea of "acid"

is so important that it is almost the only one which has filtered out from chemistry into the world without. Now acids are built up from the nonmetals. Their most striking property is that they readily unite with metals and form salts. In this one relation we have comprehended one of the important facts of chemistry, the affinity of metallic and nonmetallic elements, and their union to form the important class of substances called salts.

Studying the subject from the standpoint of the elements, it is evident that elements can act in only one way, namely, by union with one or more other elements, with the formation of compounds. Hence, union is the first reaction of chemistry, and its opposite, decomposition, follows naturally.

Three types of union occur so frequently that they should be emphasized.

Type 1. Union of hydrogen and oxygen with the formation of water. Hydrogen and oxygen stand out apart from all other elements, as water stands apart from all other compounds. They are in classes by themselves. To this idea of union of hydrogen and oxygen may be added the union of water with other compounds, especially the oxides of both metals and nonmetals.

Type 2. The union of oxygen with other elements; with metals, oxides of one type are produced, with nonmetals oxides of another. When the metallic oxides are united with water they form bases, when the nonmetallic oxides are united with water they form acids, both substances of fundamental importance.

Type 3. The union, in one way or another, of metallic compounds with nonmetallic compounds, with the formation of salts.

There are other types of reaction which may be considered as indirect union. They will be taken up as we pass along. A most helpful thought is this: that every chemical reaction is theoretically reversible, so that every type of union is balanced by an opposite action. Naturally they do not often take place at the same time. This would lead to confusion. We study and make use of changes in which one reaction only is pronounced. The equation $2H + O \rightarrow H_2O$ may be read backward, indicating that water may be decomposed into its elements. At the beginning we will avoid conditions under which such reversions take place, and usually consider a reaction in one direction only.

CHAPTER III

THE STRUCTURE OF MATTER. MOLECULES AND ATOMS

SULPHUR, water, and oxygen have been mentioned in connection with typical chemical reactions. They represent the three physical states of matter, the solid, liquid, and gaseous. From the standpoint of chemistry this difference is an incidental one, although we never lose sight of it. Chlorine, bromine, and iodine are three elements of very great chemical similarity, yet the first is a gas, the second a liquid, the third a solid. The physical state of any one of them may be more or less readily altered. Ice, water, and steam readily pass from one state to the other. For practical handling the liquid state, often obtained by solution in water, is the most convenient. But for the consideration of the structure of matter the gaseous state is the ideal condition, and from it our first ideas are derived.

If a gas is placed in an open vessel, it will be noticed that it spreads out in all directions, and presently diffuses to every portion of the room. If we are in the open, the diffusion goes on indefinitely. The gas may be heavy or light, the result is the same, although in the former case more time will be required. This diffusion will take place in spite of obstacles. As gases are not so familiar to the ordinary observer the illustration may be extended

to include volatile liquids like ether or gasoline. As they readily pass over into gases they represent the same phenomenon. Gasoline is dangerous because of its great diffusibility. If left in one place, it may fill all the surrounding space with its vapor and thus produce the danger of accidental ignition.

What does this diffusibility mean? It is most readily explained by assuming that gases are made up of little particles, called molecules, all alike, independent of each other, moving about freely with energy enough to cause them to move on and away until they meet with some barrier. This molecular hypothesis offers such a satisfactory explanation of the conduct of gases that we do not need to inquire into the physical and mathematical confirmations which can be adduced. We will assume it without anything further, except a definite summary.

Gases are made up of large numbers of small molecules, far apart as compared with their actual size, moving rapidly and freely in straight lines until they meet with an impediment, when they take another direction. The pressure exerted by a gas is due to this molecular activity. When a gas is heated the molecular activity increases, when cooled it diminishes.

Liquids are readily converted into gases, and even before they are thus converted, liquids show some properties similar to those of gases. Hence we must assume a somewhat similar structure for liquids. Gases are, roughly speaking, 500 times more diffused than the liquids from which they come. Hence it is evident that in liquids the molecules must be nearer together and their molecular activity less.

Solids are only slightly more compact than liquids, but their molecular activity must be appreciably less, as evidenced by their rigidity, and their slight tendency to give off vapor. That they possess molecular activity is evidenced by their expansion and contraction under the influence of temperature changes.

We may picture the molecular motion of a solid to be like that of people in a dense crowd. Motion is possible, but impeded in every direction. In a liquid the motion is like that of individuals in a thin crowd. Motion is rather free, but no individual can move far in any direction without meeting an obstacle. In gases the motion may be compared to that of a swarm of insects, each individual moving with great freedom and only occasionally meeting with another.

Molecules are very small. One cubic centimeter of a gas contains so many that their number is expressed by twenty figures. The common comparison of the magnified drop of water is useful for obtaining an impression of their size. If a drop of water were magnified to the size of the earth, the molecules would seem as large as baseballs. The speed of the molecules is very great. Those of hydrogen, the most rapid of all, move at the rate of about a mile a second. Others move more slowly, their speed being in the inverse ratio of the square roots of their molecular weights. Thus the oxygen molecule moves one-fourth as fast, and the chlorine one-sixth as fast as the molecule of hydrogen. When molecules meet an obstacle, either other molecules or a restraining wall, they rebound without loss of energy, that is, they are perfectly elastic. The pressure of a gas is due to the "bom-

bardment" of these molecules against the confining walls. Heat increases the motion. From certain chemical and mathematical considerations it is clear that in equal volumes of all gases under similar conditions the number of molecules is the same.

The relation of molecular motion to heat is an intimate one. When a substance is heated the speed of motion of the molecules is increased, and when we subtract heat the speed of molecular motion is decreased. The increased speed of molecular motion causes the molecules to strike harder and more often against their neighbors and the gas expands. If expansion is resisted, the pressure exerted by the gas increases, for the pressure is caused by the many blows of these molecules striking against the restraining walls. The activity of the molecules of a liquid is less than that of the molecules of a gas. If we heat a liquid, the activity at once increases, and if we continue the heat, the liquid is finally converted into a gas. A solid has still lower molecular activity than liquids: upon heating this increases, the body expands, presently melts, and finally is converted into a gas. In bringing about these changes heat is converted into molecular motion; and if the changes are reversed the molecular motion is reconverted into heat in exactly equal measure.

Water as gas, as liquid, as solid, has always the same molecules, moving more or less freely. It is apparent that the molecule is constructed of simpler units, for by chemical means we are able to break it down. The smaller constituents of the molecules are the atoms, the real units for chemical considerations, as the molecules are for physical considerations. Two or more atoms of different

elements unite to form one molecule, and chemical reactions are usually the reactions of the atoms. This has already been shown in our discussion of the combustion of carbon, sulphur, and hydrogen. The equation $C + 2\,O \rightarrow CO_2$ means that one atom of carbon unites with two atoms of oxygen to form one molecule of carbon dioxide. The equation $2\,H + O \rightarrow H_2O$ means similarly that two atoms of hydrogen unite with one of oxygen to form one molecule of water. We need some form of picture to make this real, so that devices like these are often used to represent the molecule of water.

$$\boxed{H}\boxed{O}\boxed{H};\ \boxed{H}-\boxed{O}-\boxed{H};\ H-O-H;\ O\begin{matrix}\diagup H\\ \diagdown H\end{matrix}$$

These are simply more graphic representations of the formula H_2O. They should not be studied as an end in themselves, as they may not represent true pictures; but they are often so useful, particularly the last forms, that they are practically indispensable in our consideration of the structure of a molecule.

All matter is made up of molecules and the molecules in turn are made up of atoms. In the molecule of water there are two hydrogen atoms and one of oxygen. The molecule of carbon dioxide, CO_2, contains one carbon atom and two of oxygen, and so on. These facts about molecules apply to elements as well as to compounds, for the elements are also made up of molecules. The atoms making up such a molecule are always of the same kind. Two atoms to the molecule of an element is a frequent number, so that for oxygen the formula is not O, but O_2, indicating that in ordinary oxygen the molecules contain two atoms. Ozone is an unusual form of oxygen containing three atoms to the molecule, O_3.

In general, then, O_2 is the formula to be used to represent ordinary molecular oxygen, and the written equations must frequently be doubled in order to apply an even number of atoms for the molecule. The knowledge of this fact will be assumed as understood in the following pages, although it will often seem desirable to deviate from this correct practice for the sake of simplifying the illustrations used.

THERMOMETRY AND THE METRIC SYSTEM

In all scientific discussions it is desirable to use the universally adopted units of weights and measures instead of the English units. The confusion is unfortunate, but by frequent reference to the table of comparisons the inconvenience may be minimized.

The Fahrenheit scale in thermometry registers 180 degrees from the freezing point of water to its boiling point. The freezing point was set at 32 degrees above zero, for a reason which proved quite inadequate, so that we have the unusual numbers 32 degrees for freezing, and 212 degrees for the boiling point of water. The centigrade scale assumes the freezing point of water for its zero, and the boiling point for 100 degrees, a much more natural and simple arrangement for scientific work. The transference of a temperature from one scale to the other is not difficult. One degree Fahrenheit is 5/9 of 1 degree centigrade. The only confusion comes from the necessity of adding and subtracting the arbitrary 32 degrees of the Fahrenheit scale.

The metric system of weights and measures is based upon the standard meter, one ten-millionth

part of the earth's quadrant at Paris, approximately 39.37 inches. All other units are derived from this by decimal multiplications and divisions. In simple chemical work only three sets of these measures are used.

Length. The meter, 39.37 inches=10 decimeters (4 inches) = 100 centimeters (0.4 inch) = 1,000 millimeters (1/25 inch).

Volume. The liter is a cubic decimeter. It is equal to 1.06 quarts. 1 liter (L.) = 1,000 cubic centimeters (c. c.), about 1/16 cubic inch, or 1/30 fluid ounce.

Weight. The kilogram is the weight of 1 liter of water under standard conditions. Its weight is equal to 2.2 pounds.

1 kilogram (K.) = 1,000 grams, (g.) 1/28 ounce, or 15 grains.

The most used units are the cubic centimeter and the gram. With respect to water these are equal, but for all other liquids corrections must be applied to bring them into comparison.

CHAPTER IV

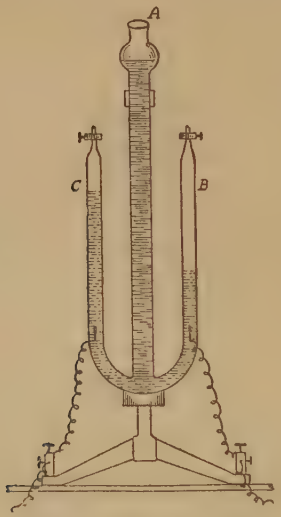
HYDROGEN, OXYGEN, AND THEIR COMPOUNDS

HYDROGEN, abundant as it is in compounds, is not familiar as an element to anyone who has not performed a few chemical experiments, nor does it occur as an element in nature in any noticeable way. In compounds, however, we find it in water, from which fact it received its name (water former). It is found in all animal and vegetable matter, which has assimilated hydrogen in the form of water. Hydrogen is found in petroleum combined with carbon. Finally, all acids contain hydrogen.

In all these compounds of hydrogen the presence of that element is only approximately apparent. One might say that gasoline seemed to contain hydrogen because it is gaseous and combustible, but hydrogen is not apparent in water or in acids, and we know of its presence there only by liberating it. In general, we may never be certain of an element in a compound judging merely from external appearances, although now and then we have some indications; lead is heavy and so are its compounds; magnesium is light, and so are its compounds. We must, however, always be cautious in drawing conclusions from such facts. When we say that water contains hydrogen, we must carefully distinguish this meaning from the meaning

of such an expression as "the water contains salt." In the one case we mean that hydrogen is a constituent, in the other case that salt is a foreign substance not strictly related to the water.

In order to obtain hydrogen in a free state we need only to select a compound of hydrogen and

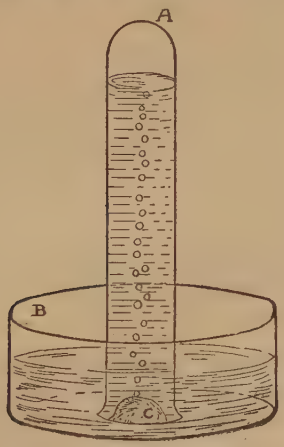


ELECTROLYSIS OF WATER

Water mixed with sulphuric acid is poured into the apparatus at *A* and the two arms *B* and *C* filled completely. When the current is passed, a gas is seen to pass from each of the electrodes and to collect above them. In a few minutes it will be seen that the one gas, hydrogen, is twice as abundant as the other gas, oxygen. The gases may be drawn off at the jets and tested.

decompose it. Water is the first to be considered and we find that water may readily be separated into hydrogen and oxygen by means of the electric current. In electricity, we constantly deal with the positive and negative conditions. Chemicals substances, or rather parts of them, are often found

to be positive or negative when in solution, and if the poles of a battery are introduced into the solution, these substances are attracted to the poles of opposite nature. Water is made up of positive hydrogen, and negative oxygen, and is therefore susceptible to electrical action. It can be electrolyzed, that is, decomposed by the current, and hydrogen will be



PREPARATION OF HYDROGEN BY THE ACTION OF CALCIUM ON WATER

The tube *A* is filled with water and inverted without loss of water in the dish *B*. When a piece of calcium *C* is placed in the water under the tube, action takes place and the liberated hydrogen rises in the tube, displacing the water.

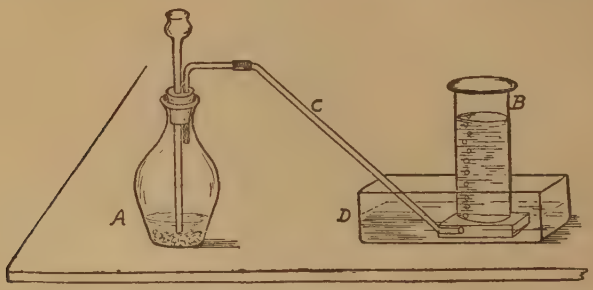
liberated at the negative pole, and oxygen at the positive pole. A simple device keeps the two gases apart. Two volumes of hydrogen are liberated and one volume of oxygen, a fact suggested by the formula of water, H_2O.

If water is brought in contact with an active metal, as calcium, this metal readily combines with the oxygen, and the hydrogen is liberated and may

be collected in any convenient way. This method is simple and clear, for not only is the hydrogen apparent, but the presence of the calcium oxide formed may readily be established.

The reaction is $H_2O + Ca \rightarrow CaO + 2H$.

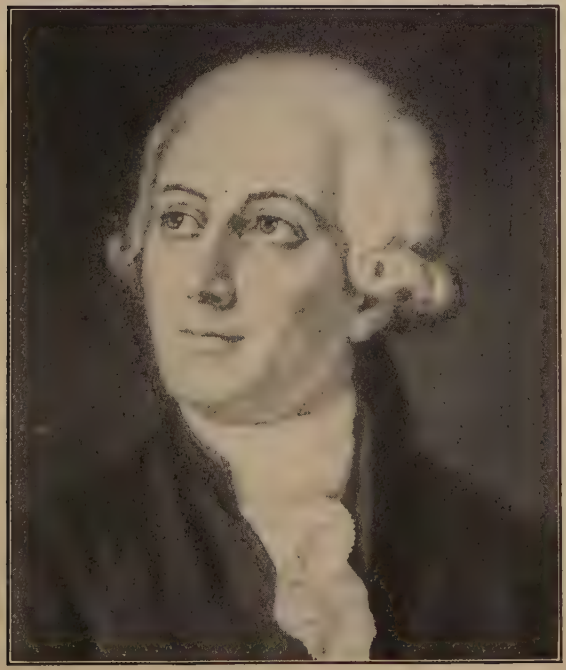
The most convenient manner of preparing hydrogen is by the treatment of an acid with a metal. Acids are made up of two parts, hydrogen and a



APPARATUS FOR GENERATING HYDROGEN AND OTHER GASES

Zinc in a convenient form (granulated) is placed in the flask *A*. It is covered with water, and sulphuric acid gradually added. The hydrogen is liberated from the acid, and on account of its great volume, passes out of the flask and is collected by displacing the water from the inverted cylinder *B*. *C* is the delivery tube and the arrangement of *D* is called a pneumatic trough.

nonmetallic part, and the latter tends to unite with active metals. Hence, when an acid is treated with a metal, it is decomposed; its nonmetallic constituent unites with the metal to form a salt, while the hydrogen originally present is left in the uncombined state, and on account of its gaseous nature escapes from the liquid in bubbles. Zinc and sulphuric acid are the substances most used for preparing hydrogen. The zinc combines with the so-called sulphate, forming zinc sulphate, while the hydrogen is liberated. The zinc sulphate may be seen as a crystalline salt



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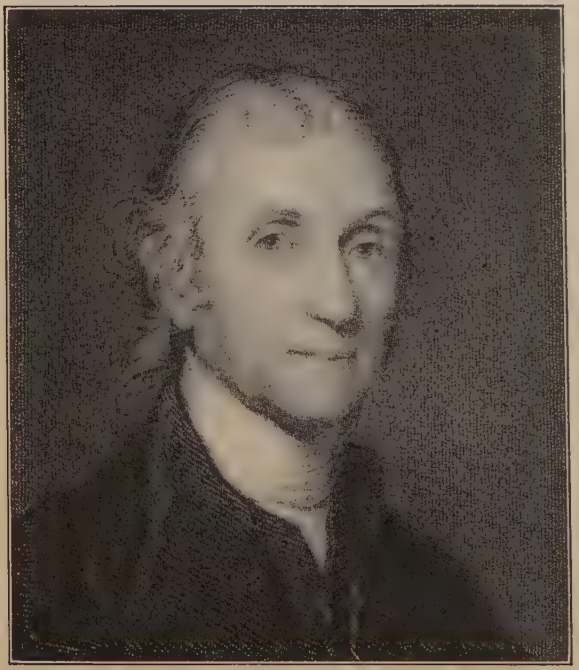

JOSEPH PRIESTLEY

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MADAME CURIE ADDRESSING A MEETING OF EUROPEAN SCIENTISTS ON THE SUBJECT OF RADIUM

if the residue from the acid is allowed to evaporate. As the gaseous hydrogen is liberated, it is conducted by tubes to inverted cylinders from which the air has been displaced by means of water. As the hydrogen enters, the water is driven out, and the cylinders are presently filled with the invisible hydrogen gas.

Hydrogen is a gas free from color and odor, not soluble in water and so light that it is used to fill balloons. It is not poisonous, but does not support life. When a flame is applied, hydrogen burns freely in the air, which means that it unites readily with oxygen, forming water in the process. The water may be seen condensing on the walls of any containers in which hydrogen is burned. This tendency to unite with oxygen is the great characteristic of hydrogen and whenever they come together they tend to unite, the product of the union being water. If hydrogen is previously mixed with air the union of hydrogen and oxygen takes place with violence. Hence in all dealings with hydrogen its mixture with air must be handled with care so that it may not become ignited. The mixture with oxygen is extremely dangerous and should be made only with the greatest precautions.

Hydrogen is the lightest substance, not alone as a gas, but also in its atom. Consequently the relative weight of all atoms is referred to hydrogen in an approximate way. The most important relation of this kind is that between oxygen and hydrogen. The ratio is 15.879 to 1. But greater convenience is obtained by making the first number an even 16 and allowing the second to deviate from unity, so that the ratio really used is 16 to 1.008.

Oxygen received its name (acid former) from the fact that it is an important constituent of acids, yet some acids contain no oxygen. It is the most important of the elements. It makes up more than one-half of the earth's crust and enters into compounds in more important ways than any other element. In particular, it is found in the uncombined form, mixed with nitrogen, in the air. The presence of such a great mass of an active element can be explained only on the ground that it exists in excess, and is left over after all possible substances have united with it.

Oxygen occurs in the combined state in water, and like hydrogen, in many plant and animal substances which are built up from water. So also many inorganic substances have water in their composition and hence contain oxygen. There are many oxides, both natural and artificial, which of course contain oxygen.

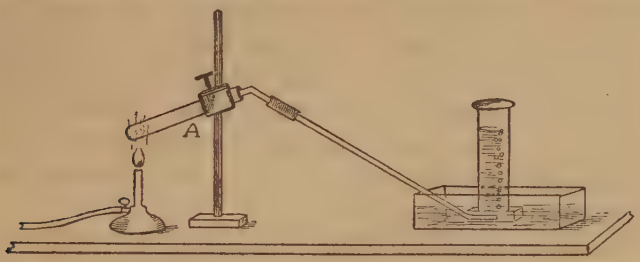
Oxygen may be prepared readily enough on a small scale by heating certain compounds which contain oxygen and decompose rather readily. Potassium chlorate is the best for laboratory purposes, and the liberation of the oxygen is facilitated by the presence of manganese dioxide. The oxygen is collected in the same way as is hydrogen, over water.

A method of no practical value, but of historical interest, is that of heating mercuric oxide. It is by this experiment that Priestly discovered oxygen, a discovery which gave Lavoisier the clue to the process of combustion, and laid the foundations of modern chemistry.

Oxygen is required by the industries on a large scale, and is prepared more economically by other

methods than those mentioned above. These are described in the chapter on industrial chemistry. The source of oxygen in these methods is either air or water.

Oxygen is a colorless, odorless gas, only slightly soluble in water. We must carefully distinguish between the oxygen which is a constituent of water,



PREPARATION OF OXYGEN

Potassium chlorate mixed with manganese dioxide is heated in the brass tube *A*. The gas passes off as it is generated, and is collected in the usual manner by passing into inverted cylinders from which the air has been displaced by water.

and which ceases to show the properties of oxygen, and the gaseous oxygen which is in actual solution. If ordinary cold water is gently heated, it will be noted presently that small bubbles appear, which consist of the air, partly oxygen, which has been in solution in the water. Water may dissolve about 1/120 of its volume, or 1/120000 of its weight of oxygen. This may seem a small amount, but it is of practical moment in that it is enough to supply fish life, and, under conditions not too unfavorable, to cause the oxidation of impurities which find their way into water.

Chemically the properties of oxygen are very striking. Anything which burns in air will burn much more brilliantly in oxygen, because there is

no diluting action due to the nitrogen. Sulphur, charcoal, phosphorus, magnesium, even iron, will burn in oxygen with a brilliant display. Oxygen unites directly or indirectly with almost every element, forming oxides, which are usually important substances. As it will unite with single elements, as carbon or sulphur, so it will unite with combinations of elements, as carbon disulphide, CS_2, provided they unite separately. The process of respiration is union of oxygen with the carbon and hydrogen originally supplied by foods. With hydrogen or gaseous hydrocarbons it unites so readily that, when a mixture is ignited, there is a very violent explosion.

Ozone is a modified form of oxygen. The ordinary oxygen molecule contains two atoms, but the ozone molecule contains three, this being indicated by O_2 and O_3 respectively. Ozone is exceedingly active, not because it contains more oxygen, but because it tends to pass over into ordinary oxygen, $O_3 \rightarrow O_2 + O$, thus liberating an oxygen atom, which is oxygen in its most reactive form.

Water. Among all the compounds which the elements form, water is preeminent. It is not alone very abundant, but its physical and chemical properties are such that it concerns a large number of phenomena in which we have the greatest interest. It would not be too much to say that its properties control the progress of chemical reaction, not alone as applied to ordinary chemistry, but as applied to the chemistry of living things, both plant and animal, and we may add to this the influence exerted by water in geological ways, in physiography and geography, and the combined influence of all these on human life.

The *physical properties* of water are exceptional. It is one of few inorganic liquids, and a liquid medium is best suited for chemical reactions, whether in the laboratory or in living organisms. It is liquid within narrow limits, 0° to 100°C., or 32° to 212° F. It has great solvent action, especially for inorganic compounds. Its solvent action on organic compounds is limited, but those having a chemical relation to water are soluble. This includes the alcohols. This great solvent power of water is very important in chemical reactions. The saying of the early chemists that substances do not react except when in solution can hardly be considered correct, but it is full of suggestion. Solution is important even when it is very slight, as in the case of marble, which reacts readily with acids. Ionic reactions, a set of reactions of the utmost importance, are dependent upon solution in water.

In other respects the physical properties of water are outstanding. It has the highest specific heat, that is, ability to absorb heat, of all substances. This influences such facts as the tempering of climates by the Gulf Stream, and enables water to be used to advantage in heating and cooling. It counts in the equalization of the temperature of the animal body. The capillarity of water also is high, illustrated by its rising in the soil from the water table below, to supply plants with moisture.

Latent Heat. When a liquid is converted into a gas, or a solid into a liquid, there is a marked increase in the activity of the molecules. This means an increase of energy, which comes from without, in the form of heat. Hence a liquid boiling away, or even evaporating slowly, or a solid melting, absorbs heat from its surroundings. In the reverse processes

this heat is given out again. The heat thus absorbed or given out by the change in molecular activity seems to be hidden, or latent, as ice water and the ice from which it is formed are both at 0°C. So also water ready to pass into steam, and the steam rising from it are both at 100°. All substances show this phenomenon of latent heat, but among them water stands very high, another fact important in the function of water in equalizing temperature.

Water contracts irregularly upon cooling. After reaching 4°C., it expands, and upon passing into ice, this expansion is so marked that the ice is lighter than water and floats. This irregularity is of the greatest importance in nature, for it results in such conditions in bodies of water, that only the upper layers freeze solid in winter, and with the varying seasons the important circulation due to changing temperatures is increased.

The *chemical properties* of water are as exceptional as are the physical. Three types of chemical reaction involving water may be mentioned, in addition to the action on substances which we ordinarily call solution. Solution is in some respects so important that it requires special treatment.

Water of crystallization. Many substances form compounds with water in which each portion seems to preserve its individuality, yet both are merged into one. In such cases the combination has a definite crystalline form, and at times another color. If the water is removed, which may easily be done, both crystalline form and color are changed.

Water of chemical union. The more active oxides of metals and of nonmetals unite readily with water. The slaking of lime, CaO, is an example. In these

cases the union is an intimate one and both constituents lose their identity. In the case of the metallic oxides the substances called bases are formed, in case of the nonmetallic oxides, the acids, both compounds of the utmost importance.

Water forms many combinations with certain double compounds, in that the hydroxyl portion, —OH, of the water unites with one constituent, and the hydrogen with the other. The double compound is thus cleft in two, and the term *hydrolysis* (cleaving by means of water) is applied to this operation. In the upbuilding of plant and animal material, and in the digestive process, this reaction is of very common occurrence.

Water by itself is rather stable, as is evidenced by its great abundance. It can be decomposed into its elements, hydrogen and oxygen, by the electric current and by excessive heat. Certain elements unite with the hydrogen, others with the oxygen, each liberating the other constituent. Finally, water is somehow decomposed in building up animal and vegetable tissue, so that often the hydrogen and oxygen are completely separated.

The composition of water has been determined with the greatest care, as the ratio of the oxygen to the hydrogen therein is the most important ratio of chemistry. It was formerly supposed that the oxygen was exactly 8 times as heavy as the hydrogen, and since the hydrogen is double, one unit or atom of oxygen would be 16 times as heavy as the single unit of hydrogen. This has been shown to be only approximately correct. The ratio is 15.879 to 1. So far as the volume relations go, it has been clearly established that the two parts of hydrogen and the one part of oxygen obtained when water is

electrolyzed, mean that the water molecule is made up of two atoms of hydrogen held together by one atom of oxygen, a condition represented by the formula H-O-H.

A number of physical properties of water remain still to be mentioned. We usually say that it is colorless, odorless, and tasteless. Water in large masses has a distinct blue color particularly noticeable in ice. The color of seas and lakes involves other features, not altogether satisfactorily explained. Pure water seems to have a flat taste, due perhaps to the dilution of the saliva, or to the lack of taste ordinarily associated with drinking water. Ordinary potable waters contain a number of foreign substances, which in ideal cases are really advantageous. These are firstly the gaseous constituents. One liter of Lake Erie water contains about 20 c. c., that is 2 volume per cent of gases. Of this about 1/20 is carbon dioxide, 1/3 oxygen, and the rest nitrogen. So far as taste and safety go these are advantageous. In fact the oxygen is the first essential for the purification of water. And this small amount is enough for waters which are not seriously defiled. Ordinary waters contain a number of solid substances, most commonly salt, acid calcium carbonate (lime), calcium sulphate, and corresponding magnesium compounds. These, in amounts not excessive, seem to be harmless, and in the opinion of many improve the flavor, though this is a matter of usage. Those used to hard waters consider the taste of soft water flat, while those used to soft waters find that the hard waters have a metallic taste. There is organic matter present, due to contact with vegetation, leaf mold and such substances. This is not in itself bad,

unless the organic matter contains dangerous bacteria. Bacterial, not chemical, pollution is the danger which menaces water supplies. Sanitary purification has for its object the removal of disease germs and turbidity, and seldom affects the mineral matter actually in solution.

Hydrogen Peroxide. Besides water, hydrogen and oxygen form another compound, hydrogen peroxide, H_2O_2. It contains in its molecule a second atom of oxygen, which is very readily split off, with the formation of a residue of water. This represents the most interesting feature of this compound, for the oxygen thus liberated is in an active form, and is effective in bleaching and disinfecting.

CHAPTER V

CARBON AND ITS COMPOUNDS.

CARBON, like hydrogen and oxygen, is met with frequently. Both as an element and in compounds it is connected with innumerable substances in common use, and its chemistry is part of the familiar happenings of everyday life. Carbon is very abundant in nature, occurring in the free state in diamond, graphite, and the various forms of coal. In combination it forms carbon dioxide, which as a gas is found in small proportions in the air, and is part of the very abundant limestone rocks. Petroleum is a mixture of compounds of carbon and hydrogen. All organic matter has carbon as its basis, as is apparent from the fact that, when charred, the black carbon may be observed. Carbon forms so many compounds of this last type that we must devote an entire subdivision of our subject, Organic Chemistry, to their study.

The *diamond* has a number of points of scientific interest. It has a distinct crystalline form, is exceedingly hard, refracts light brilliantly, and in the end is simply made up of carbon. Further, human appreciation of an object so beautiful and so rare has put this gem in a class by itself. The qualtities which make it valuable are its beauty, its durability, and its rarity. One feature of its beauty is the above mentioned high refracting power, and stones are cut in order to bring out this quality. Its great

hardness makes the diamond valuable industrially for cutting glass and stone, for which of course imperfect diamonds are selected.

The second crystalline form of carbon is *graphite*, well known as the "lead" of pencils, also called black lead and plumbago when powdered. It is often confused with lead by the unthinking, but there is no relation between them. The name graphite, "to write" refers to the quality of making a mark upon paper. Graphite is slippery to the feel, and is used as a lubricant. Its permanence—for, in spite of the fact that it consists of carbon, it burns with the greatest difficulty—enables it to be used for such purposes as stove blacking and crucibles. In recent years graphite has been made from ordinary carbon by the high temperature of the electric furnace.

That the diamond and graphite are really composed of carbon can be clearly established. Each form can be converted into the other form: even minute diamonds have been prepared from ordinary carbon. All three forms are converted into carbon dioxide upon heating in oxygen, the product being absolutely the same in each case.

This is only one of a number of instances in which we find one element appearing in a number of different forms. Such forms are called allotropic forms, and the relation between them is called allotropy. Oxygen and ozone offer such an illustration, and the various forms of phosphorus and sulphur offer others. The explanation of this is not known certainly, except in the case of ozone.

The forms of ordinary carbon are endlessly more interesting than the diamond or graphite. They consist of the various natural forms of coal, and

we may add to these some artificial forms, charcoal and coke. To understand the nature of these we will study the changes involved in the making of charcoal and apply what we learn there to the coal deposits of nature.

Charcoal is derived from wood, the chemical material of which is cellulose, with a composition represented by the formula $C_6H_{10}O_5$. If we heat wood out of contact with the air, so that there will be no burning, we will gradually drive off the gaseous constituents, hydrogen and oxygen, although in the process a considerable amount of carbon escapes in combination with them. But the bulk of the carbon will be left as the black solid, called charcoal, free from the gaseous elements of the original wood. Let us apply a similar process of reasoning to the great coal deposits of nature. Coal comes from wood tissue much as charcoal is derived in the above operation from wood, by removal of the gaseous constituents. This has taken place in the absence of air, under the influence of pressure and heat perhaps, and through long intervals of time. In the case of hard coal, or anthracite, the process is almost complete, and besides the ash (purely foreign earthy material) there is little besides carbon present. Other forms of coal may be considered intermediate between the original wood and the final anthracite. The series of products formed strikingly shows this increasing carbonization. The steps which may serve to illustrate the gradual change are: wood, 50 per cent carbon; peat, 55 per cent; lignite, 73 per cent; bituminous coal, 84 per cent; anthracite, 93 per cent. Each substance represents a decrease in the gaseous constituents, and a corresponding increase in the carbon remain-

ing. Peat plainly shows the original fiber from which it was formed, and lignite is so called because it often preserves the woody structure. There are large deposits of lignite, not so desirable as coal, but available when the coal supplies become exhausted. In the various forms of coal proper, the external resemblance to the original wood is obliterated.

We pass on now to artificial forms of carbon, and to the uses to which carbon is put in the industries.

Carbon, on account of its affinity for oxygen, burns readily, and in so doing liberates a great amount of heat. Hence it is used in its various forms for fuel, either for heat or for power.

Smoke. When hard coal burns the reaction is simple. The carbon simply unites with the oxygen of the air supplied to the fire. Carbon dioxide is formed and passes out at the flue. The ash is inert mineral matter which is accidentally present, and which is not affected by the burning of the coal. When soft coal is burned the operation is much more complex. When this coal is first placed upon the fire, the heat of the fire expels the hydrogen and oxygen still remaining in the coal, along with some carbon, and these escape as gases. As soon as they escape they become ignited and burn. As they burn, however, they are not likely to meet with a sufficiency of oxygen and in addition they are cooled. Then the hydrogen in these gases burns by preference and the carbon is liberated as soot. The prevention of the formation of soot or smoke is accomplished by the avoidance of either one of the conditions which result in smoke, namely gas formation and partial combustion. If a fuel is used containing no gaseous constituent, such as hard coal

or coke, there can be no smoke, as the carbon never assumes a finely divided form. Again, when a gas-containing fuel is used, the liberated gas, as it begins to burn, is caused to meet with enough oxygen (in the air), so that it will burn as a whole and no carbon be deposited. In practice, excess of oxygen is obtained by diminishing the amount of gas liberated at any one time. This is in its turn accomplished by means of mechanical stokers, which feed the coal into the fires very gradually. Each small installment of coal gives off no more gas than can be entirely consumed before another portion of gas is supplied.

Coke. For many purposes, particularly the extraction of iron from its ores, soft coal is unusable because of its gaseous constituents and its softening upon being heated. These defects are remedied by the preliminary conversion of the coal into coke. Coking coal is the same process as charring wood. By applying heat, the gaseous constituents, much hydrogen, some oxygen, and small portions of nitrogen are expelled, along with a considerable amount of carbon which escapes in combination with them. The coke is the residual carbon and contains the original ash of the coal. Coke is in a sense an artificial hard coal, though less compact, and serves many of the purposes of the latter.

The coke-making process has another interest besides the production of coke. The gases thus expelled are in part permanent, and in part can be condensed to liquids. The permanent gases, when properly handled, form illuminating gas, while the condensed products form coal tar. Further, among these products there is formed a considerable amount of a nitrogen compound, ammonia, NH_3.

It will be seen presently that nitrogen compounds are of unique importance, and should be preserved in every way possible. Coke making, then, has these three classes of by-products, gas, tar, and ammonia, and in the cruder methods of making coke they are wasted, as they are allowed to burn with no advantage but to get rid of them. The tendency to save these has increased in recent years, particularly under the pressure of the war. The problem is unfortunately not a simple one. It involves the installation of new and elaborate coke ovens, and, what is perhaps more serious, the establishment of a market in which these products may be sold at a sufficient profit. Sentiment alone cannot control the saving. It is necessary that close correlation be established between the different phases of the whole subject, the location of the coal, and the marketing of the various products obtained.

The greatest use of carbon in the form of coal or coke is for fuel, the burning of which converts the chemical energy into heat, by uniting the coal with oxygen. This affinity for oxygen results in another great use of carbon, the extraction of the metals. Many metals occur in their ores in the form of oxides. Hematite, the famous lake ore of iron, is iron oxide, Fe_2O_3. To obtain the iron the oxygen must be removed, and heating with carbon, usually in the form of coke, serves this purpose best. A few other uses of carbon may be mentioned. *Lampblack,* made by partial combustion of compounds rich in carbon is used as a black pigment in paints and inks. It is very durable, as at low temperatures carbon is not affected by any ordinary reagents. *Bone black* and *charcoal* are very porous, and are used for absorbents. The most striking

case of this was the use during the war of charcoal from certain sources in the gas masks. The porous carbon was very efficacious in absorbing the poison gases.

The first compound of carbon to engage our attention is *carbon dioxide*. This has been mentioned repeatedly as the product formed when carbon unites with sufficient oxygen. It occurs in the atmosphere to the extent of about 0.03 per cent, a seemingly small amount, but corresponding to a weight of 10 to 12 tons over every acre of land. Lime water exposed to the air soon shows the presence of carbon dioxide by its milky appearance. Carbon dioxide may be formed by burning carbon in air or oxygen. The latter method is practically unavailable on account of the cost of oxygen. The former has a serious defect in that four parts of nitrogen are mixed with every one part of oxygen in the air. Hence this method is used only when the admixture of nitrogen does no harm. The usual method is the treatment of carbonates, like those of calcium and magnesium, with an acid.

Carbon dioxide is a colorless gas, half again as heavy as air, in small quantities odorless; but if a full breath is taken, an odor will be distinctly noticeable. It is so soluble in water, especially under pressure, that it forms carbonated waters, which have a pleasant acid taste.

Carbon dioxide cannot burn, as it already contains all the oxygen with which it can combine. Nor do common substances burn in it, as the oxygen is so firmly held by the carbon that it will not separate from it to join other substances. With water it forms a very weak acid, called carbonic acid, but the combination is so unstable that it is

problematical whether it really exists. By virtue of its nature as a nonmetallic oxide, it combines readily with the more active metallic oxides, in the presence of water, forming the so-called carbonates. Carbon dioxide is liberated from the earth in many places, especially in springs as at Saratoga and Apollinaris, near the Rhine. Other sources by which the carbon dioxide in the air may be increased are by respiration of animals, fermentation, combustion, and decay. Withdrawal is by plant assimilation, and incorporation in the permanent rocks of the earth. There is absorption of carbon dioxide when rock disintegrates, and the carbon dioxide in the animal shells which are converted into solid rock is permanently withdrawn from the atmosphere. The influence on climate of varying amounts of carbon dioxide in the air is a much debated question. It is said that larger amounts would cause the air to become a better blanket for preserving the warmth which the earth receives from the sun. A complete loss of carbon dioxide would eliminate the possibility of life on the earth. Within the range of men's study no appreciable differences have yet been observed.

Carbon dioxide in the air brings up the question of the carbon cycle in nature. Plants are capable of absorbing this substance, and by means of the energy absorbed from the sun, to split off the oxygen, which is thus returned to the air. The carbon is built up into the plant tissue of which starch and cellulose are the most typical. We may assume that in this compound the hydrogen and oxygen balance each other, so that all the chemical energy of this substance lies in the carbon. When the animal consumes this compound for food, the

carbon is burned by the respiration process and forms carbon dioxide, which is exhaled into the atmosphere. The cycle is now complete, and is repeated indefinitely. $CO_2 \rightarrow$ C of plant tissue $\rightarrow$ animal food $\rightarrow CO_2$.

Carbon dioxide has considerable application and is made in large quantities. Its first use is for carbonated beverages. It has a pleasant taste, and being more soluble under pressure, the gas escapes when this pressure is relieved. Carbon dioxide is the leavening gas liberated in dough, either by the fermentation by yeast or by baking powders. Its importance in this case is solely because it can be conveniently generated as wanted.

Carbon monoxide, CO, is another compound of carbon and oxygen. It is formed when carbon unites with an insufficient amount of oxygen. The conditions for its formation are especially favorable in charcoal, coke, and hard coal fires, and the blue flame playing over the top of these fires is due to the final burning of the carbon monoxide formed in the lower layers. It is a poisonous gas and causes many accidents. Its greatest interest to the chemist is on account of certain general principles illustrated by its relation to the more common dioxide. The dioxide is the normal compound, formed by the complete satisfying of the affinities between carbon and oxygen. In the monoxide these affinities are only partially satisfied. Hence the monoxide tends to unite with more oxygen to form the dioxide. This is the reason why it burns. The explanation of its poisonous action is also connected with this condition. Normally the red blood corpuscles must unite with oxygen to carry this gas to the tissues. When carbon monoxide is inhaled, it attaches itself

to the red corpuscles, on account of its unsatisfied condition, and makes so firm a combination that they can no longer function with oxygen.

THE HYDROCARBONS.

Carbon unites with hydrogen to form over a thousand compounds. There is no comparable set of compounds among other elements, and this unusual variability of composition lies at the basis of the broad field of organic chemistry. The many combinations between the two elements are due to three kinds of variation.

1. There is a difference in the proportions of hydrogen and carbon present in the molecule. Such differences are shown by two sets of comparisons, C_2H_2, C_2H_4, C_2H_6, and the series CH_4, C_2H_6, C_3H_8, C_4H_{10}.

2. Although the proportions are the same, the actual amounts present in the molecule sometimes differ. C_2H_2, C_6H_6.

3. The molecules are of the same complexity, but within the molecule there are subtle variations. In a complex molecule like $C_{10}H_{16}$, it is conceivable that there might be many arrangements of the carbon and hydrogen, each arrangement resulting in a different compound.

Illustrations of these hydrocarbons are common. Marsh gas, methane, CH_4, is a constituent of natural gas. The individual constituents of gasoline, kerosene, paraffin, turpentine and coal tar "benzoles" are examples. They are gases, liquids or solids, depending upon the complexity of the molecule; C_2H_2, acetylene, is a gas: C_6H_6, benzene, is a liquid; $C_{10}H_8$, naphthalene, is a solid. They are all colorless, many have noticeable odors, and they are insoluble in

water. The great value of many of them lies in their combustibility, particularly in their being converted into gases just before burning, gasoline in carburetors, kerosene and paraffin at the tips of wicks. The liquids and solids are conveniently handled, and the gaseous condition is obtained as wanted. The benzenes have a value as being the raw materials from which coal tar products are prepared.

Organic Chemistry, to which considerable attention will be given later, is the study of these hydrocarbons and their derivatives. They form these derivatives in endless variety, by the substitution of other elements for the hydrogen. When the substituting element is a halogen, we have such compounds as chloroform and iodoform; when it is oxygen, we have the alcohols, aldehydes, and organic acids, the sugars, fats, and countless other compounds. The introduction of nitrogen gives aniline, and with many complications the important proteins. These organic compounds are so many that it is found expedient to study them apart, although, in all strictness, they involve no principles of chemistry apart from those which we are studying here.

CHAPTER VI

COMBUSTION AND ITS ACCOMPANIMENTS

COMBUSTION is only one special form of union between two substances. Our conception of a substance burning is that as it burns it gives out heat and exhibits a glowing mass. The two occurrences are intimately associated, as the glow is simply the result of the heat. We may say, then, that combustion is the union of two substances, with so great a development of heat that these substances glow. Inasmuch as one of the substances is usually oxygen, we may restate our proposition thus: combustion is the union of a substance with oxygen, with so great a development of heat that the substance glows. It may be more crudely stated thus: combustion is the union of two substances accompanied by heat and light.

We know that a fire must be "started." This means that the chemical union does not take place until the substances involved are heated. The intensity of heat required varies considerably. Phosphorus ignites when heated to a temperature just above lukewarm, and this is one reason why it is so dangerous as well as so useful. Sulphur will ignite from a small spark, carbon must be heated to a glow before it burns, and magnesium must be heated still more. We see then that before a substance burns it must be raised to a certain temperature, varying

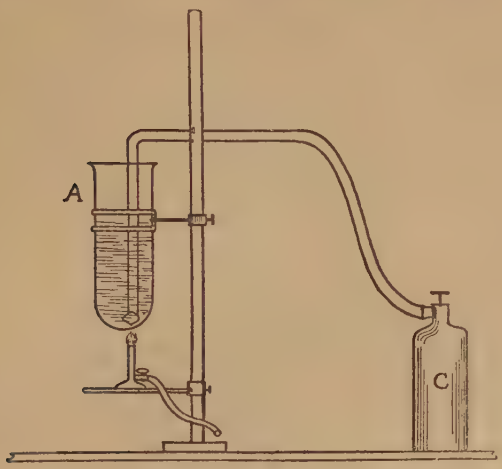
for different substances. This is called the kindling temperature.

An important factor in the readiness with which substances ignite is the size of the portion of substance which is heated. A needle and a bar of iron are of the same material, but the former is so small that when placed in a flame it is quickly raised to the temperature of its surroundings. With the same amount of heat applied the iron bar will be heated only slowly. Therefore a shaving, presenting a small mass for heating, will ignite more quickly than the block of wood from which it is cut. Magnesium ribbon ignites readily, a block of magnesium can be set on fire only with great difficulty. This idea applies particularly to gases. On account of their fine state of division a small portion is easily heated to the kindling temperature. A burning match plunged into kerosene will be extinguished, but if the kerosene is first converted to a gas, the burning match will ignite it. One great danger of gasoline lies in this circumstance. It passes off as a gas readily, and hence is in the fine state of division favorable to ignition.

We are now ready to formulate the requirements for combustion, namely, two substances with affinity for each other and the necessary temperature. One of the two substances is usually oxygen. This is nicely illustrated by the maxim of the autoist, that in order to start his engine, "he must have gas enough, not too much gas (meaning enough oxygen) and a spark." Without these three conditions there can be no combustion, with these three conditions combustion cannot be prevented. Phosphorus may be burned under water, with the greatest readiness, if the water is heated some-

what, and a stream of oxygen is directed upon the phosphorus.

It is our custom to say and to think that the various combustibles burn in the air. In a practical way this is true, because ordinarily the air surrounds the burning object, but in strict truth



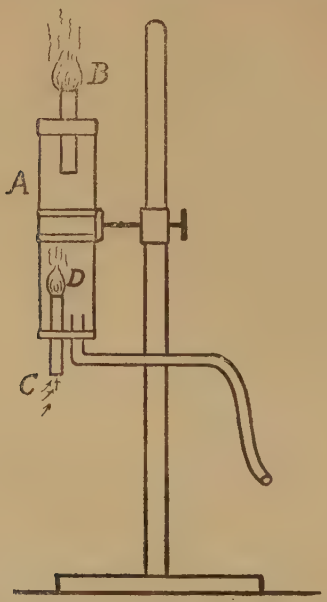
BURNING PHOSPHORUS UNDER WATER

Phosphorus may be burned under water when the three conditions of combustion are met. The water in *A* is heated to the kindling temperature of the phosphorus, and oxygen from the cylinder *C* is passed down through the water. The phosphorus burns readily.

both substances are uniting and are equally related to the action. By a little ingenuity air can be made to burn in an atmosphere of illuminating gas quite as readily as the gas will burn in the air.

Spontaneous combustion is caused by the gradual development of heat, due to some chemical change, and the accumulation of this heat until the kindling temperature is reached. Linseed oil combines with oxygen spontaneously, and in doing so develops

heat. If cloths soaked in linseed oil are carelessly packed together, they present an opportunity for such spontaneous combustion. The oil spread over the surface absorbs oxygen, and the conditions are such that the heat developed is not dissipated. The



EXPERIMENT FOR SHOWING THAT, IN THE COMBUSTION OF A GAS, THE UNION OF THE GAS AND OXYGEN IS MUTUAL

The cylinder *A* is kept filled with gas, which, passing through the tube *B*, is lighted. By using some care the upward current of air, entering at *C*, may be made to burn at *D*. In the upper flame, gas is burning in air; in the lower flame, air is burning in gas.

heat of the first oxidation accelerates a further oxidation, and this continues until the whole is hot enough to burst into a blaze.

All the methods of extinguishing combustion illustrate these three conditions. The shutting off

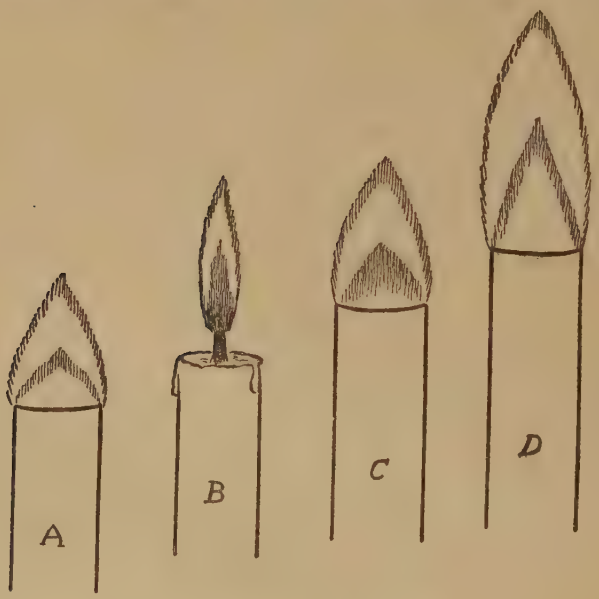
of air by smothering a fire concerns the oxygen. Water cools the burning body. Cooling is often accomplished by pulling a fire to pieces, when the loss of heat, due to radiation, exceeds the rate of heating due to the burning. Blowing out a candle flame is successful in part because of cooling, but mainly because the burning gases of the flame are blown away from the wick where the new gas supply is being generated. No matter how it is done, it will be seen that it is the removal of one of the essential conditions which is the cause of the cessation of the combustion.

FLAME

A frequent accompaniment of combustion is flame. To understand flame we need only to compare the burning of charcoal with the burning of wood. In the former case there is a steady glow, in the latter the lambent flame. We know that the difference between the two materials is simply in the gaseous content of the wood. We see therefore that ordinary flame is a burning gas. The burning of kerosene in the form of a flame is preceded by its gasification. Sulphur vaporizes before it burns. Hard coal often shows a flame, which is due to the burning of the gaseous carbon monoxide formed before the final combustion. Unless a gas is present the combustion takes the form, as in charcoal, of a steady glow.

The simplest flame is that of burning hydrogen. It shows a conical form, the interior of the cone consisting of the hydrogen emerging from the jet, the rest of the cone consisting of the burning hydrogen, glowing on account of the heat liberated. If we now consider a flame of ordinary illuminat-

ing gas, composed of carbon and hydrogen, we see that the flame is more complex. In the interior is a region of unaffected gases. On the exterior is a



A COMPARISON OF FLAMES

A, the hydrogen flame. The inner cone represents hydrogen not yet burning, the outer cone the hydrogen in the process of burning. *B*, the candle flame, which is similar to the flame from burning oil. The brown inner region represents gases which have not yet begun to burn. The luminous portion is the cone of partial combustion, luminous on account of the glowing carbon. At the bottom and around the entire flame is the region of complete combustion, shown by the blue flame which in the upper regions is difficult to distinguish. *C*, The ordinary gas flame, essentially the same as *B*. *D*, the Bunsen flame, in which the middle zone of partially burning gases is eliminated.

region, inconspicuous, of complete combustion, where everything is finally combined with oxygen. Between is a region wherein the combustion is partial. The hydrogen burns, leaving the carbon

for a moment in a free condition, and it is the glow of this free carbon which makes the flame luminous. If a cold object is placed in this middle region, some of the unburned carbon will be deposited upon it. In the case of the kerosene flame or of the candle flame, the matter is complicated a bit further, for here the gas must first be generated by the action of the heat on the fuel. When the flame is burning regularly, its heat develops a constant supply of gas from the oil or paraffin.

These features of the candle flame may be appreciated by noting the following points. The cold candle wick requires some time to ignite, because the gas must first be formed by the heat of the taper. If the flame is extinguished, it will be noticed that, for a moment, while the wick is still hot, gases are evolved, and may be lighted at some slight distance above the wick. The gases from the interior of the flame can be conducted out of the flame by means of a tube and burned as they escape from the exit of the tube. If a piece of paper is pressed down on the candle flame for just a moment, it is unaffected immediately above the wick, as the gases there are not burning; it will be coated with soot immediately around this, on account of the free carbon in the middle region; it will be charred in a circle due to the heat from the combustion, mostly in the outer region.

LUMINOSITY OF FLAME

The luminosity of a flame is ordinarily due to the glowing of a solid. In ordinary flame the solid is carbon, liberated for an instant from its compound before it is burned to carbon dioxide. Hydrogen burns with a nonluminous flame, as there

is no solid present. Methane (natural gas) CH_4 includes a proportion of carbon too small to give much luminosity. The same is true of the two alcohols, wood and grain, CH_4O and C_2H_6O, which are used for fuel just because they liberate little carbon. Acetylene, C_2H_2, on the other hand, has so large a proportion of carbon that it burns with a brilliantly luminous flame. Any gas which is to be used directly for illuminating purposes, if not already rich in carbon, must be enriched by the introduction of compounds high in carbon content. The modern solution of this problem, however, is the introduction of the mantle, made of certain metallic oxides. The gas is burned with an abundance of air, the flame being virtually a Bunsen flame, and very hot, all the energy of the fuel being directed to the development of heat. The light is obtained by the glowing of the mantle, the whole arrangement being more or less ideal, if only the mantles were not so fragile. The magnesium light owes its brightness to the glowing of the magnesium oxide formed. The various forms of electric lighting, too, owe their effectiveness to the glowing of a solid, but here the heat is obtained by physical means, not by chemical means, as in the flame.

THE BUNSEN FLAME

The Bunsen flame owes its efficiency to the introduction of a current of air at the base of the burner. The reaction of the ordinary gas flame is, as was shown above, divided into two steps, with consequent spreading out of the flame and of the heat effect. The air introduced in the Bunsen burner results in the elimination of the middle region of the flame, so that the gas burns at once, with a smaller

flame, and the heating effect is concentrated in time and space. The result is a smaller, hotter flame, which does not deposit carbon. The difference when the air holes are closed is apparent at once. The Bunsen burner is probably the most useful piece of chemical apparatus which we possess and is adapted to gas burners, even oil burners, in a variety of forms.

COMBUSTION OF ELEMENTS AND COMPOUNDS

When an element burns, it unites with oxygen. When a compound burns, each element present unites with oxygen. Carbon disulphide in burning forms carbon dioxide and sulphur dioxide. Methane burning forms carbon dioxide and water. The combustion may be interfered with, as happens so often in the case of carbon and hydrogen compounds, by lack of oxygen or by cooling. But if these conditions do not apply, all the elements are completely oxidized. When an element is present which has a low affinity for oxygen, as nitrogen, the more active elements burn, and the nitrogen is simply left in the uncombined state. The practical effect of these facts is that no matter what compound of carbon, hydrogen, oxygen, or nitrogen may be oxidized, either by rapid burning or by the slower process of decay, the final result is the same, viz., carbon dioxide, water, and free nitrogen. Hence burning is a final way of disposing of organic rubbish. The combustion products are unnoticeable and are normal constituents of the atmosphere.

EXPLOSIONS

Explosions are often the result of very rapid combustion, and hence may be considered here. The

simplest case is the explosion of a mixture of hydrogen and oxygen. We know that when hydrogen and oxygen combine much heat is liberated by the union. When hydrogen burns at a jet, a very small portion burns at any one moment, and the heat therefrom is dissipated as fast as it develops. If, however, the hydrogen and oxygen are mixed previous to lighting, the union takes place with great rapidity throughout the mass, and all the heat of union is developed instantaneously. The result of this is an expansion of the water vapor formed, so great, and so sudden, that the disruptive force is tremendous.

It is generally assumed that volatile liquids like gasoline and ether are explosive. This is a misconception, for they are ordinarily stable substances. Their evil reputation for explosiveness results from their volatility and their combustibility. They are, on account of the former fact, likely to form a mixture with the air, and if this mixture is lighted we have a repetition of the conditions mentioned above —a sudden development of heat, resulting in a violent expansion of any gaseous matter present, water vapor, carbon dioxide and the nitrogen of the air.

The same effect is accomplished by other conditions in the use of the old-fashioned gunpowder, a mixture of charcoal, sulphur and potassium nitrate, KNO_3. When the powder is lighted, the charcoal and sulphur burn, combining with the oxygen from the unstable nitrate, and the final result is a mixture of gases, mainly carbon dioxide and nitrogen, which are highly heated by the burning. Their formation and expansion is the cause of the explosion, which is not very violent unless the gases are pent up, and suddenly burst through the confining walls.

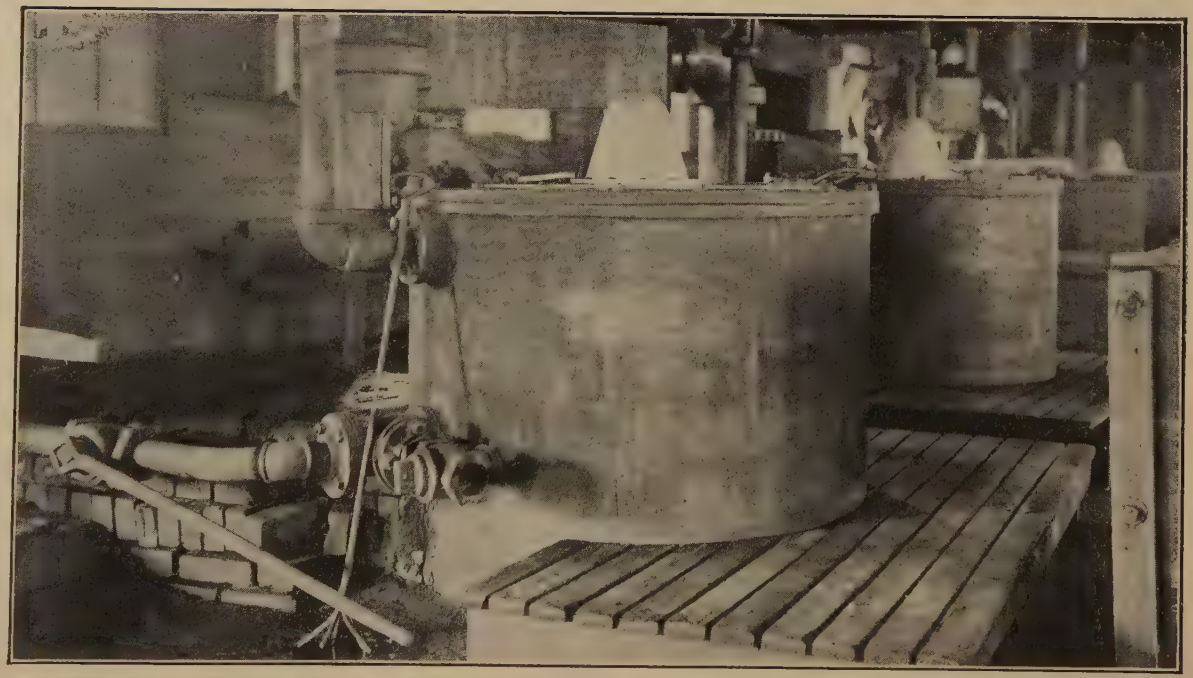
A third type of explosions is caused by the disruption of certain organic compounds containing nitrogen. This element causes the whole to be unstable and allows chemical changes to take place rapidly. The most important explosives of this type are: nitroglycerin, $C_3H_5(NO_3)_3$; guncotton, $C_6H_7O_2(NO_3)_3$; picric acid, $C_6H_3O(NO_2)_3$; and trinitrotoluol, $C_7H_5(NO_2)_3$. It will be noted that these all have a somewhat similar composition. The nitrogen causes them to be unstable, the oxygen can unite with the hydrogen and carbon, and everything concerned is within the same molecule, so that the decomposition takes place with the utmost suddenness. The first of the above may be taken as typical. It decomposes as follows: $2C_3H_5(NO_3)_3 \rightarrow 6CO_2 + 5H_2O$ (gaseous) $+ 6N + O$, which means that nitroglycerin is changed instantaneously from a compact liquid into a voluminous mixture of gases. The violence of the disruptive force is due to the suddenness of the gas formation, and this in turn to the fact that all the reactions occur at infinitely small distances, all within the same molecule.

CHAPTER VII

NITROGEN, AIR, AND NITROGEN COMPOUNDS

HYDROGEN, oxygen, and carbon are generally considered the first three constituents of organic matter. Nitrogen enters as a fourth into the composition of compounds like the proteins and their derivatives. These four are therefore naturally classed together, not for their chemical similarity, but because of this relation to the products of living matter. Nitrogen does not rank among the most abundant elements of the solid earth, yet it is so available in the air that as an element and in its compounds it is very conspicuous in our lives. It makes up four fifths of the air, but is less noticeable there than the more active oxygen. When we do develop the process of converting the free element into its compounds, we will not lack for a supply. Nitrogen compounds are not abundant among the minerals, but soils contain small amounts, and the Chile deposits of sodium nitrate, $NaNO_3$, are enormous. The latter are nevertheless appreciably depleted by the vast inroads made upon them. The chief organic compounds of nitrogen are the proteins, the main constituents of animal tissue. The chemical changes in these proteins in the processes of digestion, assimilation, and excretion lead to

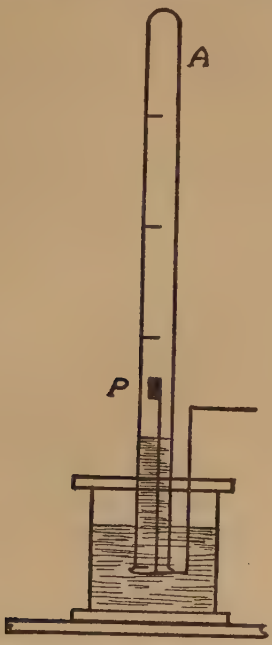
BUREAU OF MINES RESCUE CREW, EQUIPPED WITH OXYGEN BREATHING APPARATUS



NITRATION ROOM WHERE COTTON IS TREATED WITH NITRIC ACID AND SULPHURIC ACID IN THE MANUFACTURE OF EXPLOSIVES

other nitrogen compounds of especial interest to the physiologist.

Nitrogen may be prepared readily from the air by the removal of the oxygen. For this purpose



EXPERIMENT SHOWING THE PREPARATION OF NITROGEN FROM AIR AND ALSO THE PROPORTIONS OF OXYGEN AND NITROGEN IN AIR

The tube *A*, filled with air, is inverted over the dish of water. A piece of phosphorus, *P*, is introduced, and in the course of twenty-four hours all the oxygen present unites with it. The resulting oxide of phosphorus dissolves in the water, and only nitrogen remains. It will be seen that one-fifth of the air has disappeared.

phosphorus may be burned in a closed volume of air. As it unites with the oxygen, the white fumes of the oxide of phosphorus appear. They may be made to go into solution in water, when the nitrogen

will be left, showing the properties which are already familiar from an acquaintance with the air. It is a colorles, odorless gas, slightly lighter than air, and slightly soluble in water. Chemically it is inert, combining directly with rather few substances. When a combination is established, it is usually unstable, simply because the nitrogen in it has a low affinity for the other constituents. Compounds which are unstable and reactive are of the utmost importance from the chemical standpoint. Stable substances may have their uses, but they are not the substances with which the chemist accomplishes his results; nor would they be best suited to the delicate changes necessary in the vital tissue of plants and animals. Nitrogen compounds exhibit great instability and reactivity, and in the composition of foods and of explosives they are of great importance. So great a place have these two features assumed that "the nitrogen question" has a permanent place in chemical interests. The essential point of the question is the fixation of nitrogen, namely the converting of the inert gas nitrogen into compounds which men can use. On the whole, the tendency of nitrogen is toward the free condition, in which state it is useless. Nitrogen once in combination should be carefully preserved in that condition, and a regular new supply of nitrogen compounds established, by the methods of manufacturing and of agriculture.

THE AIR

The air is not a compound of nitrogen and oxygen, but a mixture. This fact is apparent from a comparison of the properties of air with those of compounds of nitrogen and oxygen. The latter have

characteristic properties, essentially different from those of their constituents, while air has simply the properties, somewhat toned down, of each of the constituents. When air is liquefied the nitrogen evaporates much more readily than the oxygen, and a separation may thus be readily accomplished. If air were a compound it would act simply as one unit.

The composition of air may be determined by carefully subtracting the oxygen from a known volume of air, and measuring the remainder. Air is thus found to consist of 21 per cent by volume, or 23 per cent by weight of oxygen. In all ordinary considerations of air the 1 per cent of argon present is not noticed. In fact it escaped detection until the year 1894, when Rayleigh and Ramsay discovered it. The discovery of a new constituent of air, present in such large amounts, made a great sensation and has stimulated research in that general direction. As a result a number of similar gases have been found in small amounts, all with somewhat the same properties as argon. Argon is inert, and so far has not been found to combine with any other substance, or even with itself. In the molecule of argon there is only one atom.

In the atmosphere there are normally found water and carbon dioxide besides the oxygen and nitrogen. The water content is very variable, the content on a cold day and on a warm day being very different. At —10° C. (14° F.) saturated air consists of about 0.2 per cent water; at 30° C. (88° F.) it may contain six times as much. It should be remembered that air is dry or damp, not in accordance with the amount of water which it holds, but in accordance with the amount of water it is still capable of taking up. The carbon dioxide, three parts

in ten thousand, 0.03 per cent, is rather constant in open spaces, but in closed spaces, where animals are breathing or fires burning, the increase in the proportion may be marked. No harm, however, can be directly attributed to the increased amounts ordinarily met with.

Liquid air is prepared in considerable amounts for the purpose of obtaining oxygen and for producing low temperatures. In many cases the nitrogen in these processes is wasted, but uses for it may develop in the future. The principle of making liquid air is a combination of pressure and cooling. Cooling is accomplished by the expansion of air previously compressed, for the expansion of a compressed gas results in cooling much as does the evaporation of a liquid. Liquid air is a colorless liquid, which evaporates with great rapidity, and in doing so abstracts heat from anything with which it comes in contact. The Dewar flask, familiar as the thermos bottle, is used to hold liquid air, for the vacuum between the two walls of the flask prevents the entering of heat. The temperature of liquid air under ordinary pressure is about —170°C. (—300° F.). The nitrogen, being more volatile, boils away first, and presently liquid oxygen is left as a pale blue liquid.

Nitrogen combined with Hydrogen. Ammonia, NH_3, is formed with some difficulty by the direct union of the two elements, and the ammonia of commerce comes from very indirect sources. It is a light gas of well-known odor. The gas is familiar, but since it is usually handled in its water solution, called aqua ammonia, or ammonia water, and rather incorrectly, ammonia, the fact may not generally be appreciated that it is a gas. The strong solution

at ordinary temperatures holds from 300 to 400 volumes of the gas.

One great use of ammonia is in artificial freezing. Ammonia is rather easily converted to a liquid by pressure and ordinary cooling, such as by running water. This liquid ammonia can be caused to evaporate rapidly, for it is normally a gas. It then ab-

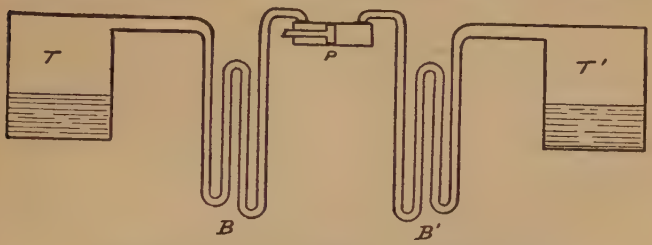


DIAGRAM OF THE AMMONIA ICE MACHINE

T and *T'* are the tanks in which the liquid ammonia is placed. It is taken from these tanks and returned to them alternately. *P* is the pump by which the ammonia is withdrawn from one tank and forced into the other, in the first case accelerating evaporation and cooling, in the second reconverting the gas to the liquid for the next operation. The chilling of the expanding gas is applied by means of the coils, *B* and *B'*, alternately.

sorbs heat rapidly and has therefore intense cooling effect. This is not peculiar to ammonia, but ammonia is the most convenient of the gases of this type. When ammonia is converted to a liquid, its latent heat is allowed to dissipate into the air or into cooling water. When the liquid reverts to a gas, the containers are so arranged that it takes its latent heat from the object which is to be cooled. The diagram will show how this is accomplished.

Liquid ammonia is contained in the tank T, and by means of the pump P the gas is withdrawn from above it, causing rapid evaporation, and hence rapid absorption of heat. Refrigeration is accomplished by allowing the pipe conducting the cold ammonia

gas to chill the spaces or objects to be cooled. For making ice this pipe chills a salt solution stored in great tanks. This brine will not freeze until chilled to about —20° C. (0° F.). Into this brine square cans of distilled water are suspended until their contents are frozen solid. As the gas is pumped out of the tank T it is forced into the tank T'. In this compression process the heat which it has just taken up is again liberated, and is carried away by ordinary cooling means, running water for example. At the end of the operation the apparatus is ready again, in inverse order, for another freezing operation, the liquid ammonia now being accumulated in T'.

Ammonia has one chemical property in which it differs from all other common substances. It combines directly with water thus, $NH_3 + HOH \rightarrow NH_4OH$, properly written $(NH_4)OH$, because the so-called ammonium group acts like a single atom of a metal. The compound, called ammonium hydroxide, is very similar to sodium hydroxide, caustic soda, or lye, and it is used similarly for cleansing purposes. It is, however, much milder in its action. Ammonia also unites directly with acids to form salts, very similar to those of sodium. In all these combinations, ammonium, NH_4, acts like the single metal atom, sodium.

Nitrogen combined with Oxygen. Nitrogen forms a series of compounds with oxygen. These illustrate very nicely the law of multiple proportions. With the same amount of nitrogen present in each of these compounds, the oxygen increases in regular steps.

1. Nitrous oxide, N_2O.
2. Nitric oxide, N_2O_2, more correctly NO.
3. Nitrous anhydride, N_2O_3.
4. Nitrogen peroxide, N_2O_4 (or NO_2).
5. Nitric anhydride, N_2O_5.

Nitrous oxide is a colorless gas, which is the well known "laughing gas" of surgery. The second compound is remarkable in that it, a colorless gas, unites directly on contact with oxygen, to form NO_2, which is of a strong brown color. The readiness with which these two pass into each other by gaining and losing oxygen, is distinctly unusual, and causes them to be used as carriers of oxygen, especially in the manufacture of sulphuric acid. The gas with less oxygen takes oxygen from the air to form the peroxide. The latter surrenders oxygen to sulphur dioxide SO_2 converting it to the trioxide SO_3, itself being reduced to NO. On further contact with air this again forms the peroxide, and thus the process continues, as long as oxygen is supplied.

The most important of these oxides is the fifth, nitric anhydride. It is so called because with water it forms nitric acid, which is the chief of all nitrogen compounds. By itself it is hardly more than a curiosity. The chief interest centers in the nitric acid.

Nitric acid is a colorless liquid, but unless mixed with considerable water, decomposes gradually and becomes yellow. The yellow color is then indirectly a sign of high concentration, and fuming nitric acid, as it is called, is a very powerful and dangerous reagent. Nitric acid has for its greatest use the making of explosives. The essential point of these explosives is that the molecule is capable of disintegration, with the consequent formation of gases. To disintegrate, a molecule must be unstable, and the presence of nitrogen is the readiest way of accomplishing instability. The common explosives contain either the nitrate, NO_3, group, or the nitro, NO_2, group. Both are introduced by treating the

original substance with nitric acid mixed with sulphuric acid. The latter negatives the effect of the water which is formed as a by-product.

Nitric acid is also used as a source of oxygen, for it decomposes readily, as do most nitrogen compounds. It will not readily yield pure oxygen, but is convenient for adding oxygen to other compounds.

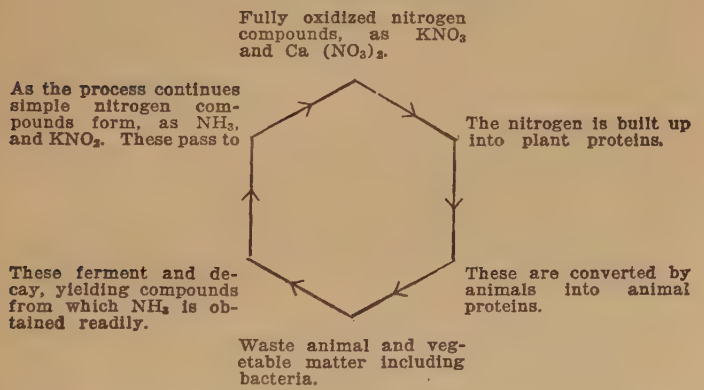
A discussion of an acid is not complete without some mention of the salts which the acid forms. The salt has the same structure as the acid, but the hydrogen is replaced by a metal. HNO_3, nitric acid, is readily converted into KNO_3, potassium nitrate, or $NaNO_3$, sodium nitrate, or $AgNO_3$, silver nitrate, and so on. These salts as a class have three main applications: They supply oxygen to other substances, as does HNO_3, and upon this fact the use of potassium nitrate in gunpowder is based. They supply nitrogen for fertilizer purposes. Sodium nitrate is the salt used almost exclusively for this. They form convenient soluble compounds with the metals when the metals are desired in combination; as silver nitrate, $AgNO_3$, in electroplating.

The necessity of nitric acid in making military and engineering explosives is one of the features which has given rise to the nitrogen question. The other is the need by plants of nitrogen in the combined form. Nitrogen compounds for explosives must be in the form of nitric acid or a salt thereof, and when the explosive is used, the nitrogen is liberated as free nitrogen. Hence the compounds used for these purposes must always be replenished. For many years the natural deposits of sodium nitrate in the north of Chile have supplied this need, and the supply will last for some time still. But in time of war, when it is most needed, this over-

seas supply might readily be shut off. Hence much attention was given during the recent war to the fixation of nitrogen, and large plants were built where it was proposed to form nitric acid on a large scale.

For agricultural purposes nitrogen in practically any compound is available, for one compound passes readily over to another. This will be best illustrated by a diagram showing the nitrogen cycle.

THE NITROGEN CYCLE.


Fully oxidized nitrogen compounds, as KNO_3 and Ca $(NO_3)_2$.
As the process continues simple nitrogen compounds form, as NH_3, and KNO_2. These pass to
The nitrogen is built up into plant proteins.
These ferment and decay, yielding compounds from which NH_3 is obtained readily.
These are converted by animals into animal proteins.
Waste animal and vegetable matter including bacteria.

The nitrogen compounds of any ordinary type will fit into this cycle and serve their purpose. It would seem possible that when once there were nitrogen compounds in sufficiency, the cycle would be maintained and the agricultural needs always provided for. There are, however, many sources of loss, such as farm waste, decay under unfavorable conditions, and fire, and in all these the nitrogen escapes, so to speak, from the cycle. There are ways by which the atmospheric nitrogen is drawn into this cycle, to a slight extent by electric discharges in the atmosphere, more by the fixation of

nitrogen by leguminous plants. Most people know of the beneficial effect of growing and plowing under a field of clover. Nitrogen fixation has for one of its objects this replenishing of the nitrogen compounds for agricultural uses.

The methods which have been applied for nitrogen fixation are several.

1. Uniting the oxygen and nitrogen of the air by means of electric discharges. This has been profitable only where water power is available for the generation of the electricity. Such conditions obtain in Norway. Lower oxides are first formed; these pass over on the addition of oxygen (of the air), water, and lime into calcium nitrate. This can be converted into any desired form.

2. The cyanamide process consists in causing free nitrogen to combine with calcium carbide. This compound may be used to supply the soil with nitrogen capable of absorption by plants, or ammonia, NH_3, may be obtained from it and applied thus, or converted into nitric acid.

3. Under conditions not easily attained, nitrogen and hydrogen can be directly combined to form ammonia. This is the synthetic Haber process. The ammonia may be applied as a fertilizer, in the form of a salt. For purposes of making explosives, it must be oxidized and thus made into nitric acid. Both these steps represent great achievements of modern chemistry. The results are accomplished along the lines of "greatest resistance" so to speak. The chemical chances of success are not large, but slight as they are, they have been used as the basis of successful manufacturing processes.

4. The last of the more important methods is, strictly speaking, not a method of fixation, but of

saving the small proportion of combined nitrogen which is stored up in coal. Soft coal is destructively distilled in large amounts for making coal gas and coke. The nitrogen present escapes as ammonia, and if this is all saved the total is considerable. For explosives the ammonia must be oxidized as in the synthetic ammonia process. Most of the ammonia now obtained in this manner is devoted to agricultural needs.

CHAPTER VIII

SULPHUR AND ITS COMPOUNDS

SULPHURIC acid from the standpoint of the industries is probably next to water the most important compound, and a study of chemistry can make little progress without a knowledge of its properties.

Sulphur, the element, is well known. It can be obtained in several allotropic forms. If sulphur is heated to its boiling point and cooled suddenly by pouring into water, it takes on a gummy form which only slowly reverts to the original brimstone. Sulphur occurs free in nature, in spite of the fact that it is reasonably active. Its occurrence free is due to recent formation and more or less accidental protection from union with oxygen and metals. In Louisiana the sulphur occurs several hundred feet below ground, and is brought up in the molten condition accomplished by forcing down superheated steam. As sulphur melts at 114° C., it requires a temperature above that of ordinary steam to liquefy it.

Sulphur is found also in combination with metals. Sulphides of copper, mercury, zinc, and lead are very important ores. Their value lies usually in the metals which they contain, yet the sulphides of iron and zinc are used as sources of sulphur for making sulphuric acid. It also occurs in a number of abundant sulphates; as Na_2SO_4, $CaSO_4$, and $MgSO_4$, sulphates of sodium, calcium, and magnesium.

The physical properties of sulphur are familiar. There is one popular misconception, namely, that concerning the odor of the element. Its odor is almost inappreciable, but when burned the odor of the oxide formed is very noticeable, and this is usually attributed to the sulphur itself. Chemically, sulphur is marked by two affinities, that for metals and that for oxygen. The former is often the cause of the tarnish of metallic objects, especially silver. It accounts for the sulphide ores in nature, and is the cause of many difficulties in the preparation of metals for the industries, as the presence of sulphur is usually injurious. Its affinity for oxygen results in the formation of the much-used sulphur dioxide, SO_2, and sulphuric acid, H_2SO_4.

The uses of sulphur are for making the old-fashioned black powder, and similar pyrotechnic mixtures; for making spraying solutions for fungicides; for vulcanizing rubber; and especially for making its oxygen compounds.

HYDROGEN SULPHIDE, H_2S

This gas is not formed directly by union of hydrogen and sulphur, as the affinities are not sufficiently strong. It is prepared indirectly by the simple reaction between iron sulphide and sulphuric acid. It is a colorless gas, with a fetid odor, known to those who have visited sulphur springs. Such spring waters contain the gas, since it is markedly soluble in water. The gas burns readily, as might be expected, forming sulphur dioxide and water. Hydrogen sulphide is a much used laboratory reagent, as it forms characteristic compounds with many of the metals. The differences in these

compounds lie in their varying colors and solubilities, so that by its means many of the metals may not alone be detected in the form of compounds, but these compounds may be separated from one another. It is an indispensable laboratory reagent.

SULPHUR DIOXIDE

When sulphur burns in the air or in oxygen, gaseous sulphur dioxide is formed. It is colorless, but when formed in this way traces of the trioxide give it the familiar bluish cloudy appearance. It is rather soluble in water and forms with the water an acid called sulphurous acid. When, however, this acid is formed in considerable amounts it breaks down into water and the dioxide. Hence such a solution acts indifferently as either sulphur dioxide or sulphurous acid. The great characteristic of sulphur dioxide, as also of sulphurous acid, is its tendency to unite with another atom of oxygen, forming sulphur trioxide and sulphuric acid respectively. There is no essential difference, for sulphur trioxide with water forms sulphuric acid. To this chemical activity is attributed the bleaching and disinfecting action of sulphur dioxide, although it is likely that much of it is due to union not with oxygen, but with other constituents of the color or the bacteria. By far the greater portion of sulphur dioxide prepared in the industries is simply as an intermediate product in the manufacture of sulphuric acid, to which we will now turn our attention.

SULPHUR TRIOXIDE AND SULPHURIC ACID

Sulphuric acid is at the basis of practically all acid industries. It would be included in the list of the substances without which the recent war

could not have continued. In the report of a national commission appointed to study and watch the chemical industries in connection with the war, sulphuric acid receives first place. Its structure, preparation, and properties should therefore be fully understood.

Sulphuric acid may be said to be made up of sulphur trioxide and water. $SO_3 + H_2O \rightleftarrows H_2SO_4$. It may be separated into these two constituents with some precautions, and this feature of its structure frequently asserts itself. The exact formula of sulphuric acid is, $\begin{matrix} H-O \\ H-O \end{matrix} > S = O$. This shows how the various atoms are held together in the molecule. It indicates that the molecule is a unit, yet that the hydrogen is directly held to oxygen only, as in water, and sulphur to oxygen only, as in sulphur trioxide. In the great majority of reactions, however, in which sulphuric acid takes part, the so-called sulphate group (SO_4) remains intact. The hydrogen is readily displaced by metals and sulphates formed. For such reactions the formula H_2SO_4 represents the structure best.

The reactions of sulphuric acid which enter into simple relations are three.

1. The possibility of decomposing into water and sulphur trioxide, and subsequently losing oxygen. When heated with substances which have affinity for oxygen, this reaction takes place.

2. Sulphuric acid has a striking affinity for water. This is noticeable whenever the two are mixed, for much heat is developed. So much, in fact, that care must be exercised and thorough mixing accomplished in order to distribute this heat through the mass. As a result of this affinity

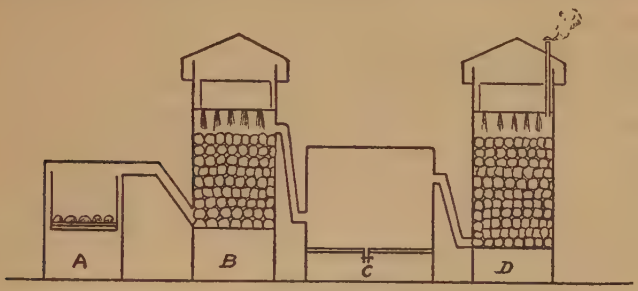
the acid absorbs water vapor from air and other gases which may be passed through it. It extracts water from substances which contain water, either free or combined. And it even extracts the hydrogen and oxygen from many substances such as sugar, as though they were really present as water. It is used for this reason in the making of explosives. The making of explosives depends upon the action of nitric acid upon certain organic compounds, and water is a by-product. The water thus formed would dilute the nitric acid and diminish its action, and sulphuric acid is therefore added to absorb this water. During the war one-third of all the sulphuric acid manufactured was used for such purposes.

3. The third and most important reaction of sulphuric acid is its marked acid action, that is, its tendency to form sulphates with metals and metallic compounds. The list of these reactions is a long one and they are applied in many ways. They are all alike in that the hydrogen of the acid is in each case replaced by the metal involved. In simple cases, when the metal is free, the hydrogen escapes free, but in every other case it combines with that which had been in combination with the metal.

Since sulphuric acid is the fundamental acid it must be prepared in some fundamental way. Other acids can be prepared from it, but sulphuric acid itself must be derived from some original source. Hence its preparation is unique.

It has already been stated that this acid is made up of sulphur trioxide and water, $SO_3 + H_2O \rightarrow H_2SO_4$. The addition of water presents no difficulties, so that the problem is to prepare the sulphur trioxide.

When sulphur or certain abundant compounds of sulphur are burned the sulphur unites with oxygen to form sulphur dioxide, $S + 2O \rightarrow SO_2$. The addition of one atom of oxygen to this yields the sulphur trioxide, and it is this step which presents the only



THE CHAMBER PROCESS FOR THE MANUFACTURE OF SULPHURIC ACID

In *A* sulphur or a compound of sulphur is burned with an abundant supply of air, and sulphur dioxide is thus formed. The mixture of sulphur and dioxide with a great excess of air (oxygen) is passed upward through the tower *B*, which accomplishes several purposes. This tower is filled with inert material, down which the desired liquids are made to trickle in fine streams. Among the uses of this tower is the cooling of the gas, sulphur dioxide, the introduction of the nitrogen oxide catalyzer and of water. *C* represents one of a number of chambers, in which the union of oxygen and sulphur dioxide takes place, followed by the union of the resulting sulphur trioxide with water. Steam is introduced here, to supply an abundance of water. The sulphuric acid thus formed is drawn off from the bottom of the chamber. When the nitrogen introduced in the air becomes excessive, the desired reactions cease to take place, and the remaining gases are passed out through the tower *D*, where the useful oxides of nitrogen are in great part recovered. The walls of the chambers, connections, and towers, are lined with sheet lead, which is affected comparatively little by the acid.

real difficulties. It is accomplished by the help of catalyzers by one of two methods.

(1) *The Chamber Process.* In this process sulphur dioxide, air (oxygen), nitrogen peroxide, and steam are allowed to react on each other in huge leaden chambers. The oxide of nitrogen acts as an oxygen carrier, in that it first yields oxygen

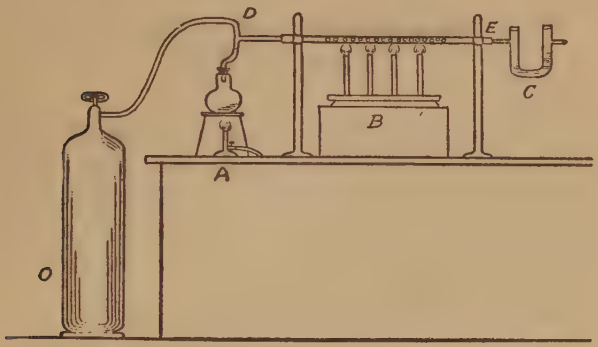
to the sulphur dioxide, and immediately recombines with an atom of oxygen from the air present. It is now ready to oxidize another molecule of the sulphur dioxide. This continues indefinitely, until the nitrogen of the air accumulates in excessive amounts, when the residue is allowed to pass out of the system. The sulphur trioxide formed at once unites with water to form sulphuric acid, which settles to the floor of the chamber, and can be drawn off. This contains an excess of water, which must be expelled by evaporation. In the manufacture of such a basic substance the engineering features are very prominent. The operation must go on on a large scale; it must be continuous; there must be a minimum of waste; heat must be economized; by-products must be recovered; the handling of the acid is difficult. The making of sulphuric acid is a vast affair, and a chamber system covers much ground. Yet all the details are worked out to such perfection that this process, elaborate as it is, is carried out with certainty of success and the product is placed upon the market at a price so low that the acid may be used as raw material in many other industries.

(2) *The contact process* is much simpler. The sulphur dioxide mixed with air passes over heated catalyzers, finely divided platinum being very serviceable, and the two are thus caused to unite. Catalyzers are easily injured by foreign matter, which is likely to be present in the sulphur dioxide, and this presents the chief difficulty in the method. The sulphur trioxide is then united with water to form the acid.

Sulphuric acid is a heavy colorless liquid which flows in a sluggish stream. Hence it presents the

appearance of an oil and is often called oil of vitriol. It dissolves in water in all proportions.

The first characteristic of an acid is its power to form salts with metals, and such a typical acid as sulphuric acid shows this property in a marked degree. Most metals form salts with sulphuric



THE CONTACT PROCESS FOR MAKING SULPHURIC ACID

Sulphur dioxide generated in the flask, *A*, is mixed at *D* with oxygen from the cylinder, *O*. The mixture passed over the heated platinum catalyzer in *B*, and the two gases are now combined to form sulphur trioxide, which may be shown by disconnecting at *E*. The sulphur trioxide may be passed into the water in the U tube *C*, and thus converted into sulphuric acid.

acid. Sodium sulphate and iron sulphate are types. They are usually well crystallized salts, with color only when the metal introduces color. The typical sulphate of sodium has the formula Na_2SO_4. If, however, only half the amount of sodium is applied, the acid salt, sodium hydrogen sulphate, is obtained, $NaHSO_4$, half acid and half salt, and partaking of the properties of both. This acid salt is a crystalline solid, with a sour taste and a regular acid action. It is often very useful in that it represents sulphuric acid in a solid form.

CHAPTER IX

THE REMAINING NONMETALLIC ELEMENTS

THE common nonmetallic elements number twelve. Of these five have already been considered. There still remain the four halogens, fluorine, chlorine, bromine, and iodine, besides phosphorus, boron, and silicon. It will not be advisable to discuss more than the main features of these seven.

THE HALOGENS

The halogens have received this name, meaning salt formers, because they unite with the metals in a simple manner to form salts, Na+Cl=NaCl, sodium and chlorine=sodium chloride, common salt.

Fluorine, although rather abundant in nature, is of minor moment for our purpose. The other three present an excellent example of a group of elements, in which the resemblances are very striking, and what differences there are, very regular. Such a group bears very definitely on the question of the origin of the elements. Their resemblances and differences are of such a regular nature that we simply cannot accept as final any idea that different elements have no ultimate connection.

The three elements of this group occur in nature in somewhat similar manner, in compounds only, and frequently associated. Their properties show

their relationship in that the three elements are very similar, or when they differ, vary in a regular way. The physical state is characteristic and is suggestive of all their relations. Chlorine is a gas and is the most active; bromine is a liquid and comes next in activity; iodine is a solid and is the least active of the group. The atomic weight of bromine, 80, is a mean between those of the other two, 35.5 and 127. The color of chlorine is marked, that of bromine more so, and that of iodine still more. The affinity of all for hydrogen and the metals is very great, but it varies in the regular order. Chlorine has the greatest affinity, and will remove hydrogen or a metal from combination with the others. Bromine ranks next. The affinity for oxygen is of the reverse order, that of iodine being greatest. So regular are all these properties, that a knowledge of any two of these elements would enable us with great certainty to tell the properties of the other. Fluorine is a fourth member of this group, coming before chlorine. Its properties are such as one would expect from its position.

Chlorine, the most important of the group, is a heavy greenish yellow gas of great chemical activity. Its affinity for hydrogen is comparable with that of oxygen, and a mixture of hydrogen and chlorine explodes with some violence when ignited. They even unite under the influence of strong light, and hydrogen will burn in an atmosphere of chlorine. This affinity results in the use of chlorine for bleaching and disinfecting.

Organic substances are usually colorless. Only such have color as possess a rather complicated structure. If therefore a colored substance loses any of its constituents, or they are altered in any

way, the new substance is likely to be free from color. Most colored substances are made up of carbon, hydrogen, oxygen, and often nitrogen. The easiest of these to remove is hydrogen, so that any substance likely to unite with hydrogen may be a bleaching agent. Hydrogen peroxide, through the active oxygen which it supplies can act thus, but chlorine is the most used. Its action is simple, in that it simply withdraws some hydrogen from the coloring matter, and the residue is colorless. Chlorine needs water for a catalyzer, else it cannot bleach. The by-product of bleaching with chlorine is hydrochloric acid, HCl, an injurious substance, hence bleaching is often accomplished by means of bleaching powder, made by adding chlorine to lime. It is as effective as chlorine.

The action of a disinfectant is probably similar to that of a bleacher. Chlorine is efficient in this respect, and its use in improving public water supplies has been a great public boon. The amount used is less than one part in one million, and although its presence is sometimes noticeable and therefore objectionable, it annually saves many lives by the destruction of typhoid germs.

Bromine is less active than chlorine, but resembles it otherwise very closely in all chemical respects. It is a heavy liquid, easily convertible to a gas. It is used in medicinal and photographic preparations, the manufacture of dyes, and as a disinfectant. Its greatest use is in medicine. Iodine is still less active than bromine. It finds extensive application in the chemical laboratory and in medicine.

All the halogens form typical compounds with hydrogen. Hydrochloric acid is easily the most important. It is a fairly heavy gas, very soluble

in water, and it is this aqueous solution which is used in the laboratory. It is an active acid responding in all respects to the tests applied to acids. It is prepared with ease by treating sodium chloride with sulphuric acid, and collecting the gaseous hydrochloric acid in water. The commercial acid is known as muriatic acid.

The halogens have a low affinity for oxygen, but with precautions all but fluorine can be brought into combination with it. These compounds are unstable, and for that reason useful. $CaOCl_2$, bleaching powder, is of this nature, and readily gives up its oxygen or its chlorine according to conditions. Potassium chlorate, $KClO_3$, is another oxygen compound of chlorine, valuable because on heating it yields oxygen.

PHOSPHORUS

Phosphorus is striking on account of its great affinity for oxygen. Its compounds are of vital importance in plant and animal growth. Otherwise the characteristics of the element and its compounds conform to nonmetals in general. Phosphorus may be prepared in two allotropic forms, the red and the yellow. It will be recalled that oxygen, carbon, and sulphur may also occur in different allotropic forms. The yellow form of phosphorus is the form usually associated with that element. It is a waxy solid, igniting with great ease and burning violently, on account of its great affinity for oxygen. Phosphorus pentoxide, a solid, is formed as a white cloud, and hence phosphorus was often burned for the formation of smoke screens during the war. The glowing of phosphorus when exposed to the air is usually attributed to its slow oxidation. Yellow phosphorus must be kept under water, partly be-

cause of this slow oxidation, and partly because of the danger of its becoming ignited. The other form of phosphorus, the red, is much less active. It may be handled freely and is not poisonous as is the yellow. Yet when ignited it burns fiercely. Each form may readily be converted into the other.

The most interesting use of phosphorus is for friction matches. The match of forty years ago consisted of a stick of wood upon the end of which a bit of yellow phosphorus was placed. Hence these matches glowed in the dark. When rubbed, the heat of the friction was sufficient to ignite the phosphorus, and the combustion was communicated to the wood by means of a coating of sulphur. Later matches improved greatly upon this arrangement, particularly in the elimination of the sulphur, which gave off the disagreeable odor of sulphur dioxide when burned. The modern match involves the following features: The tip consists of a phosphorus compound (sometimes phosphorus sulphide, but its exact composition is a trade secret), held by means of glue to the stick. A layer of paraffin carries the fire to the wood and the wood is powdered with a mineral substance to quench any spark after the match is extinguished.

The safety match is ingenious. Its effectiveness is based upon the fact that red phosphorus and potassium chlorate produce a very inflammable mixture. For the purposes of safety the red phosphorus is placed upon the friction surface of the box and the potassium chlorate, mixed with some combustible substance, as antimony sulphide, is placed upon the match. The match therefore ignites only when rubbed on the special surface.

The problem of obtaining a fire must have been an important one in the olden days, before the time of friction matches, as it is now if there are none of these available. The ancient stories of Prometheus and his stealing the sacred fires of heaven and the cult of the Vestal Virgins are illustrations of the importance of this matter. The obtaining of fire by the friction of two sticks is probably still used in many remote regions. Only recently have matches begun to drive out the custom in the Philippines, and flint and steel were in use not so long ago in those islands. There have been a number of interesting chemical methods contrived for obtaining fire, among them the contact of a mixture of sugar and potassium chlorate with sulphuric acid.

Many compounds of phosphorus are very interesting. Phosphine, PH_3 is comparable with ammonia, NH_3. It is a poisonous gas, highly inflammable. The oxide of phosphorus, phosphorus pentoxide, has a striking affinity for water, so much so that it may be used for drying gases and for extracting water from such substances as sulphuric and nitric acids. When united with water it forms an acid in the regular way. With enough water the common phosphoric acid is formed.

From this, acid salts called phosphates are derived. Sodium phosphate has medicinal applications. Calcium phosphate is a constituent of bones, and natural phosphate rock is much used for making fertilizers.

Boron is of rather limited interest. Boric (or boracic) acid has medicinal qualities and is used for a preservative. Borax has some uses, particularly as a cleansing agent, as a flux in brazing, and a glaze in making earthenware. Borax deposits and lakes in California form the chief sources in this

country. In Italy boric acid is obtained from steam emanating from the earth.

Silicon is considered the most important element in the realm of minerals. The great bulk of the earth's crust is made up of compounds of silicon, which occur in a surprisingly large variety, all built up more or less in the same manner. Silica, SiO_2, and the silicates are not very reactive, and except in a few directions, the chemist can accomplish little with them. However, during geological processes involving high temperatures and pressures, and long periods of time, changes of a great variety were accomplished, and many different silicates formed. A short list of the most common silicates is here given.

Potassium Feldspar, $KAlSi_3O_8$.
Sodium Feldspar, $NaAlSi_3O_8$
Calcium Feldspar, $CaAl_2Si_2O_8$.
Mica, $H_2KAl_3Si_3O_{12}$.
Talc, $H_2Mg_3Si_4O_{12}$.
Clay, $Al_2Si_2O_7$ or $H_2Al_2Si_2O_8$.

They are very stable substances and only a limited number of reagents react upon them, usually at high temperatures. The glass and porcelain industries involve silicon compounds.

Silicon itself is most important as a constituent of cast iron and steel, where it plays a part similar to that of carbon. Carborundum, a valuable abrasive, is a compound of carbon and silicon, SiC. Silicon dioxide, silica, SiO_2, is the important constituent of the quartz minerals known as quartz, quartzite, agate, opal, rose quartz, amethyst, flint, and by many other names.

CHAPTER X

SYMBOLS, FORMULÆ, VALENCE, EQUATIONS

THE symbols used for the chemical elements are shown in the table of the elements. They are the initial letters of the name, frequently the Latin form, and when two elements have the same initial letter, a second characteristic letter is used. But the symbol means something more than the element. It means also one unit amount of the element, that is, an atom, with the atomic weight which characterizes that element. H means one atom of hydrogen, possessing a weight of 1. O means the atom of oxygen, with its atomic weight of 16. The symbol is often used to imply also this weight expressed in grams, a matter of some convenience. Ca + O under these conditions would imply 40 grams of calcium and 16 of oxygen.

The formula of a compound is made up of the symbols of the elements composing it, and expresses the kinds and numbers of the atoms in the molecule. The symbols of the metals are usually written first. These formulæ are more or less self-evident, but the use of numbers may be confusing. A number written before a formula modifies all the atoms in the formula. $2H_2SO_4$ indicates the whole formula taken twice. The subscript modifies the one element only. These devices are simple and with a little care are soon mastered.

ATOMIC AND MOLECULAR WEIGHTS

Atomic weights may be conveniently defined as the weights of the atoms of the elements, compared with that of the atom of hydrogen. For convenience the unit is made 1/16 of the atomic weight of oxygen, 16, because hydrogen has a weight deviating from this to a slight extent, and reference to an even number saves many recalculations. The definition just given, however, is open to criticism, as we cannot distinguish or weigh an atom. The atomic weight really represents the combining weight of the elements. If an element enters into compounds with more than one proportion, the smallest proportion is the one selected. The determination of atomic weights is one of the most carefully conducted operations of chemistry, and requires theoretical considerations as well as practical experimentation. The outcome of atomic weight determinations for ordinary purposes is that there is associated with every element a number, the atomic weight, which represents the mass which enters into all combinations. When we say that the atomic weight of oxygen is 16 we mean that for every unit of oxygen present in a compound a mass of oxygen represented by that number is present.

In the same manner the molecular weight of a compound may be defined as the weight of the molecule referred to the same unit. It is determined with readiness by adding up the atomic weights of the various atoms present in the molecule. The molecular weight of sulphuric acid is 98, obtained by adding up the atomic weights. $H_2 = 2$, $S = 32$, $O_4 = 64$. The atomic and molecular weights form the basis of all numerical considerations involving the composition of compounds.

In many reactions groups of elements pass from one combination to another without being modified. Nitric acid, HNO_3 forms potassium nitrate, KNO_3 and sodium nitrate, $NaNO_3$; the nitrate group, NO_3, remains intact; hence it is convenient to consider them more or less as units, and in many cases they are placed in parenthesis, as $Ca(NO_3)_2$, calcium nitrate. These are called radicals. The most common are SO_4, NO_3, CO_3, PO_4, OH, NH_4, called sulphate, nitrate, carbonate, phosphate, hydroxide and ammonium respectively.

VALENCE

The formulæ of certain compounds, HCl, (hydrochloric acid), H_2O, (water), NH_3, (ammonia), and CH_4, (methane), make it clear that the four elements, chlorine, oxygen, nitrogen and carbon have unequal combining power as measured by hydrogen. This varying combining power, as illustrated by these elements, varies from one to four. This is called the valence of the elements, and in all formulæ and reactions it must be considered. The valence of an element is its combining power, (quantity, not intensity) compared with that of hydrogen. The simplest way of determining this valence is by considering the hydrogen compounds, when the valence is apparent at a glance. But it may be determined from other combinations as well, especially from those with oxygen, which has a valence of two. From the formulæ K_2O, CaO, Al_2O_3, CO_2, it may be seen that the valences of the elements combined with oxygen are respectively, 1, 2, 3, and 4, as these valences will be required to balance the total valence of the oxygen.

Radicals have definite valences, determined by the residual valence of their constituents. In the SO_4 radical, the four oxygen atoms have a valence of eight, the sulphur of six, hence two are unprovided for, and this residual valence is the valence of the group. This is confirmed by the fact that the group combines with two hydrogen atoms, forming $H_2(SO_4)$. When it can be measured against hydrogen, valence is always easy to determine.

In spite of its simplicity the idea of valence is sometimes difficult for the beginner to grasp. The matter will be considered only when necessary, but all formulæ and equations must be written in strict conformity to its requirements.

Valence is sometimes variable. Sulphur shows a valence of four in SO_2, and of six in SO_3. Copper has a valence of one in CuCl, and of two in $CuCl_2$. This may seem to introduce uncertainty into the whole matter. But such is not the fact. We may say simply that when sulphur has an abundance of oxygen available it will unite with three atoms. The compound formed will be SO_3, and the valence of the sulphur will be six. When, however, there is a dearth of oxygen, sulphur will unite with only two atoms, and its valence will be four. The same reasoning applies to the copper and chlorine and all similar cases.

EQUATIONS

Equations have already been used as necessity has demanded, and to make the ideas of the subject clearer. Two forms of expression are used:

$$NaCl + KNO_3 = NaNO_3 + KCl, \text{ and}$$
$$NaCl + KNO_3 \rightarrow NaNO_3 + KCl.$$

The latter is often the more convenient, as it indicates more than mere equality, and by reversal

of the arrow it can be made to indicate the opposite reaction.

$$NaCl + KNO_3 \leftarrow NaNO_3 + KCl.$$

Further when both arrows are used,

$$NaCl + KNO_3 \rightleftarrows NaNO_3 + KCl,$$

it indicates that the reaction is reversible, that is, may go in either direction, according to conditions.

In equations there must be a numerical balance of all the atoms. In using an equation to express a reaction it must first of all indicate the facts, the valences must be properly considered and the equation must balance. These equations are of great value for checking up reactions, for explaining them, and for suggesting new ideas. For example, the equation

$$Zn + H_2SO_4 \rightarrow ZnSO_4 + 2\,H.$$

Zinc + sulphuric acid → zinc sulphate + hydrogen

represents a common reaction between a metal and an acid. If instead of the metal zinc we apply its oxide it is easy to see what becomes of the additional oxygen.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O.$$

Zinc oxide + sulphuric acid → zinc sulphate + water.

Or if zinc chloride is used, the reaction is easy to follow;

$$ZnCl_2 + H_2SO_4 \rightarrow ZnSO_4 + 2\,HCl.$$

Zinc chloride + sulphuric acid → zinc sulphate + hydrogen chloride.

These equations are lacking in that they indicate nothing concerning the energy transformations. This information is sometimes supplied thus:

$$2\,H + O = H_2O + 68{,}000 \text{ calories.}$$
$$H + I = HI - 6{,}000 \text{ calories.}$$

These equations indicate that in the formation of water from its elements 68,000 calories of heat are

developed, while in the second case the union of hydrogen and iodine absorb heat. The amounts applied are the atomic weights called for by the symbols, respectively 2 and 16 grams in the first, forming 18 grams of water. In the second fig. 1 gram of hydrogen and 127 grams of iodine unite to form 128 grams of hydriodic acid.

Further, these equations do not indicate that the reactions must necessarily take place. If the reaction does take place it does so in accordance with the given equation, but it is not a mathematical necessity.

CALCULATIONS

The simpler calculations of chemistry are based upon atomic weights, formulæ, and equations. If we rewrite one of the above equations, introducing the atomic and molecular weights, some of the numerical relations may be made clear.

$$\underbrace{Zn\ O}_{65,\ 16}\ +\ \underbrace{H_2\ S\ O_4}_{2x1,\ 32,\ 4x16}\ \rightarrow\ \underbrace{Zn\ S\ O_4}_{65,\ 32,\ 4x16}\ +\ \underbrace{H_2\ O}_{2,\ 16}$$

$$\underbrace{}_{81}\qquad\underbrace{}_{98}\qquad\underbrace{}_{161}\qquad\underbrace{}_{18}$$

Zinc oxide is thus seen to be 65/81 zinc, and 16/81 oxygen, and calculations may be made accordingly. Should the question arise how much zinc sulphate could be formed from a given amount of zinc oxide or sulphuric acid, we need only consider the above values in a proportion.

$$\frac{ZnO}{ZnSO_4} = \frac{81}{161} = \frac{\text{known amount zinc oxide}}{\text{unknown amount zinc sulphate}}$$

or

$$\frac{H_2SO_4}{ZnSO_4} = \frac{98}{161} = \frac{\text{known amount of sulphuric acid}}{\text{unknown amount of zinc sulphate}}$$

This method lends itself to all possible combinations and is at the basis of all the calculations of analysis and manufacturing.

OXY-ACETYLENE WELDING AS APPLIED TO REPAIRING STEEL STRUCTURE WORK AND SHIPS

Copyright, Ewing Galloway

STILLS AT AN OIL REFINERY

NOMENCLATURE

Although the system of nomenclature used in chemistry is far from ideal it is simple and serviceable enough. For ordinary purposes the following principles apply.

Compounds containing two elements are given names ending in "ide," as sodium chloride, NaCl; calcium oxide, CaO. A metal is uniformly mentioned first. In case of nonmetals the element which seems to be of the greater interest is first mentioned. There are exceptions to this rule for "binaries" in such substances as sodium hydroxide, Na (OH); ammonium chloride, (NH_4) Cl; sodium cyanide, Na(CN); but in each of these the group in parenthesis may be looked upon as a unit, acting as though it were a single element. The names are sometimes reversed, so that we hear "chloride of sodium" and "oxide of calcium." But there is no other change.

When there is more than one combination of the same elements numbers are often used, as carbon monoxide CO, and carbon dioxide CO_2. Sulphur dioxide SO_2, and sulphur trioxide SO_3, nitrogen trioxide N_2O_3, and nitrogen pentoxide N_2O_5. Other ways of differentiating are also used, which often have no recommendation except custom. However, a name like hydrogen peroxide, H_2O_2, is suggestive as implying that this compound contains more oxygen than the usual oxide of hydrogen, water. So also a name like silver suboxide suggests that the compound contains less than the normal amount of oxygen. In general a suffix, "ous," indicates less, and "ic" more of the element considered secondary in the

compound, as cuprous and cupric chloride, CuCl and $CuCl_2$.

Acids are named in respect to their containing oxygen or lacking oxygen. In the former case they are classed as oxy-acids, HNO_3, and in the latter as hydro-acids, HCl. The oxy-acids are named after the nonmetal present, the ending of the name indicating the relative amount of oxygen. The name ending in "ic" is used for the most important acid, as sulphuric H_2SO_4, nitric HNO_3, carbonic H_2CO_3. The salts from them are called by names ending in "ate," as sulphate, nitrate, carbonate. The modifications of this for other cases are best shown by a table.

The common acid, $HClO_3$, chloric acid; its salt, $KClO_3$, potassium chlorate.
With more oxygen, $HClO_4$, perchloric acid; its salt, $KClO_4$, potassium perchlorate.
With less oxygen, $HClO_2$, chlorous acid; its salt, $KClO_2$, potassium chlorite.
With still less oxygen, HClO, hypochlorous acid, its salt, KClO, potassium hypochlorite.

Like the names of the first group, these are sometimes reversed, so that we may say chlorate of potassium. Names like "chlorate of potash" are unscientific, but are usually readily understood.

The hydro-acids are simply named, hydrochloric, hydrobromic acid, and so on, according to the nonmetal contained in them. Their salts, as NaCl, fall into the first group and are named after the manner of sodium chloride.

Many substances like ammonia NH_3, and methane CH_4, have specific names which are used to the exclusion of any names based upon their composition. They apply usually to familiar substances and cause little trouble.

CHAPTER XI

CHEMICAL REACTIONS

IF any progress has been made by the reader in the understanding of the characteristics of the elements and their compounds so far discussed, the nature of chemical reactions must to a certain extent now be familiar to him. The first conception may not be an easy one, but after the first comprehension progress should be rapid. Chemical reactions vary less than might be supposed at first glance, and it is the purpose of this chapter to classify and analyze them.

The simple reactions which come under the scope of inorganic chemistry may be placed in one of four classes.

(A) Union of elements and compounds.

(B) Decomposition into elements or simpler compounds.

(C) Withdrawal of one constituent from a compound through its greater affinity for another. This reaction often takes the form of the replacement in a compound of one element by another element of similar nature.

(D) Ionic reactions among acids, bases, and salts, including double decomposition.

CHEMICAL UNION

Union among elements and compounds is a familiar experience in the laboratory, and a few

experiments would make the idea clearer than much explanation. Some cases of union are familiar, such as combustion, a reaction in which the element burning unites with oxygen to form the respective oxide. Corrosion of metals is another illustration. Metals unite with oxygen or sulphur to form simple compounds. A union may be so rapid that we call it a combustion, or only moderately rapid, so that it requires some minutes perhaps, or again so slow that in short periods of time its action is imperceptible, as in the tarnishing of metals.

The essential features of such a union are that the elements cease to exist as free elements; they are merged into a new substance with a set of properties differing from those of its constituents. The compounds contain the elements, but in a chemical sense, not as a bottle contains a liquid, or sirup contains sugar. The element is not usually apparent in its compound. Unless some special tests are applied, neither carbon nor oxygen is noticeable in their compound, carbon dioxide. The union of simple compounds to form more complex compounds is of somewhat similar nature. The constituents, as in the case of elements, are merged into the new substance and lose their own characteristic properties. The union of water with oxides of metals and nonmetals represents the most characteristic phase of this.

The convenient signs by which a chemical union, in fact any chemical change, may be recognized are: the development of heat, although in some cases heat is absorbed; the appearance of a new set of properties; the fact that proportions involved are absolutely definite. When these facts are noted, we may be

certain that the change which has taken place is of a chemical nature.

All chemical changes are theoretically reversible and we can hardly conceive of such reversion being impossible. It is true, if ordinary conditions favor one reaction, they must ordinarily be altered materially to favor the opposite. Hence in most simple discussions one phase of a reaction is likely to be all that demands our attention.

DECOMPOSITION INTO ELEMENTS AND SIMPLER COMPOUNDS

This is the opposite of the reaction of union. Naturally another set of compounds is ordinarily to be discussed in cases of decomposition. For union we select our illustrations from active elements like phosphorus and magnesium. For decomposition mercuric oxide and nitrogen compounds, both unstable, offer good illustrations. This difference applies to union and decomposition involving compounds instead of elements. Sulphur trioxide and calcium oxide unite readily with water to form more complex substances. But the reverse kind of change is illustrated by carbonic acid and mercuric hydroxide.

$$H_2CO_3 \rightarrow H_2O + CO_2.$$
$$Hg(OH)_2 \rightarrow HgO + H_2O.$$

THE WITHDRAWAL OF ONE CONSTITUENT FROM A COMPOUND

Several reactions of this type have already been referred to. When water is treated with calcium, the affinity of the calcium for the oxygen is so great that it extracts the oxygen from the water, combining with it, and the hydrogen is left

free. Copper oxide when heated with carbon loses its oxygen to the carbon and the copper is left in uncombined form.

$$H_2O + Ca \rightarrow CaO + H_2.$$
$$CuO + H_2 \rightarrow H_2O + Cu.$$

Replacement. An interesting case of replacement is that of the action of one of the more active metals with an acid. The metal replaces the hydrogen, and the latter is freed. This is the regular method of preparing hydrogen.

IONIC REACTIONS AMONG ACIDS, BASES, AND SALTS

These are of such a special type that they will require special treatment in a later chapter.

The topic of chemical reaction would be incomplete without a reference to *catalyzers*. These are substances which accelerate a reaction which would otherwise ultimately be completed, but at a slower rate. At the end the catalyzer is found to be unaltered. So striking is the difference in speed of reaction at times that the catalyzer seems actually to cause the change to take place. The reason for the action of catalyzers is often not clear, but several types are fairly well understood. Many catalyzers include elements which have a variable valence. It is possible, and in some cases certain, that these elements take up an additional amount of oxygen from the air, for example, thus passing to their higher valence. They then lose this oxygen to some other substance, dropping to the lower valence. This may be repeated indefinitely. Oxides of cobalt, manganese, cerium, and nitrogen are in this group.

Another group of catalyzers is supposed to act through the formation of intermediate compounds,

which are again decomposed and the catalyzer is left in its original state. Such a supposition is plausible enough, but can be verified in few cases.

Still another catalyzer is the metallic, often called the contact catalyzer. Palladium and platinum are especially efficient. These act in the case of gases particularly. It is supposed that they absorb the gases by a process called occlusion. The gases are thus brought into such intimate contact within the minute spaces of the metal that they come within the sphere of their natural chemical attraction.

Water is an important catalyzer. In fact it acts more often than we ordinarily suspect. Chlorine is said to bleach, but the presence of water is essential. The substances called enzymes, active in the digestive juices, may be classed among the catalyzers. This carries us into other chapters of our subject, but they should be mentioned in this connection. A small amount of the enzyme brings about the change in a large amount of food. Ferments, too, are similar in their catalytic action, but since they are living organisms, explanation of an altogether different type is possible.

"Negative catalyzer" is a term applied to substances which retard the rate of action of other substances. They may actually have a retarding effect, or in a sense nullify the action of positive catalyzers. They do not compare in importance with the catalyzers of the type mentioned above.

EQUILIBRIUM OF CHEMICAL REACTIONS

The general idea of equilibrium in a physical sense will be illustrated from the case of a bottle partially filled with ammonia water. We will first imagine the stopper of the bottle to be in place.

Ammonia gas escapes from the water into the space above. Presently this space becomes saturated, and ammonia passes back into the water at as rapid a rate as it leaves it. We now have a state of equilibrium, the rate of action in one direction balanced by the rate in the opposite direction. There are abundant proofs that this condition is not one of rest. It is simply balanced action.

If now the stopper of the bottle is removed, the ammonia gas in the space above the water will escape into the air, and its amount in that space diminishes. The equilibrium is now disturbed, and more ammonia escapes from the water in an attempt to fill up the space, but from the space the gas will continuously pass into the air. In this manner the ammonia will finally all pass from the water. If, on the other hand, more ammonia gas were forced into the bottle, the equilibrium would be disturbed in the other direction and the gas would pass into the water to the limit of its capacity. This simple physical example is cited to make clear the same idea applied to chemical reactions. Reactions of the double decomposition type are of such a nature that equilibrium is the first condition, and, unless there is some disturbance of this equilibrium, there is no progress in the chemical reactions. If we mix solutions of sodium chloride and potassium nitrate, we might readily assume that there would be formed two new substances, sodium nitrate and potassium chloride. Then, if we begin with the latter two, they will react to form the first two. The result is an equilibrium. The equilibrium will remain, and all four substances will be present unless we find some means of disturbing it, by pushing it in one direction or the other. There are two simple

devices, akin to the ammonia water device, of removing one of the products from the reaction.

One of these devices is to so select our substances that one of the products is a gas, or can readily be converted into a gas, which will then escape from the solution. The reaction between calcium chloride and sulphuric acid is such a case, $CaCl_2 + H_2SO_4 \rightarrow CaSO_4 + 2HCl \uparrow$ (a gas). The hydrochloric acid formed escapes from the mixture on account of its gaseous condition and has no further action. The reaction cannot reverse; the arrow pointing upward indicates the escape of the gas.

The other device is the selection of substances so that one of the products is insoluble in the water present, hence it is just as truly removed from the reaction as though it were a gas. The insoluble substance precipitates and its escape would be indicated in an equation by an arrow pointing downward.

$CaCl_2 + Na_2CO_3 \rightarrow 2NaCl + CaCO_3 \downarrow$ (an insoluble solid)

Simple as this matter is, it is an essential consideration in the progress of chemical reactions. Some important industrial methods, like the Solvay soda process and the Haber ammonia process, have become possible by the full appreciation of the conditions of equilibrium.

CHAPTER XII

THE LAWS OF MOLECULES AND ATOMS—SOLUTIONS

IT is evident that gases resemble each other fairly closely. A more exact study reveals the fact that in certain physical considerations all gases are quite alike. They obey the same laws, and, it will be seen presently, have the same physical composition. The gas laws concern pressure, temperature, and diffusibility.

THE LAW OF PRESSURE, BOYLE'S LAW

Gases are made up of molecules moving rapidly through the empty spaces lying between them. The molecule is small in comparison with the spaces in which it moves. The expansion and contraction of a gas does not involve the molecules proper, but only the spaces between them. When pressure is applied to a gas, the distance between the molecules is diminished, while it increases when the pressure is relieved. This diminution or increase of volume is perfectly regular, depending directly upon the change in pressure, and is the same for all gases, whatever their nature. This fact is expressed formally by the law: other conditions remaining constant, the volume of all gases varies inversely as the pressure. This is expressed also by the formula

$$\frac{P}{P'} = \frac{V'}{V.}$$

Pressure is measured conveniently on the basis of the column of mercury, 760 mm., or 30 inches high, which balances the weight of a column of air of indefinite height at sea level. This unit of pressure is one atmosphere, or 760 mm., and is expressed in English units as 15 pounds to the square inch. Under ordinary conditions, near sea level, the pressure may be ordinarily assumed to be one atmosphere, or 760 mm. A given volume of any gas will just double its volume if this pressure is cut down one-half, or it will contract to half volume if the pressure upon it is increased to double.

THE LAW OF TEMPERATURES—CHARLES'S LAW

The addition of heat to a gas increases its molecular activity and the gas expands. Withdrawing heat, that is cooling, diminishes its molecular activity and the gas contracts. It is found that the amount of expansion and contraction for all gases is directly proportional to the changes of temperature. The law may be stated formally as follows: all gases expand or contract equally, in direct proportion to the increase or diminution of the absolute temperature. Formula:

$$\frac{V}{V'} = \frac{\text{abs. } T}{\text{abs. } T'}$$

This increase or diminution is 1/273 of the volume of the gas, starting at 0° C. for every degree warmed or cooled. In order to make comparisons we must use a scale for temperature measurement which has an actual meaning, for the ordinary scales are arbitrary, starting at a zero point determined solely by convenience. The absolute zero is at a point 273° below that of the centigrade scale, and it is determined as follows: When a gas which is at

0° C. is cooled 1° C., its contraction is 1/273 of its volume. Cooled 10°, the contraction is 10/273 of its volume. Hence, cooled to —273°, the contraction is 273/273. Its volume is now zero. As contraction is due to decrease of molecular motion, the seeming contraction to zero indicates a cessation of all molecular motion. The point at which this condition exists, —273° C., is therefore a real starting point of molecular motion, that is, of temperature. On the absolute scale, then, 0° C. equals 273° Abs., and room temperature, 21° C., is 294° Abs. Temperature comparisons for volume changes must be made on this absolute scale, which is obtained by adding 273 to the temperature on the centigrade scale.

THE LAW OF DIFFUSION—GRAHAM'S LAW

Gases diffuse into space at unequal rates, but according to the same law. It can easily be seen that a heavy gas will diffuse slowly and a light gas rapidly. Hydrogen, with a molecular weight of two (there are two atoms in the molecule), will diffuse more rapidly than oxygen, molecular weight thirty-two. It will, however, diffuse only four times as readily, instead of sixteen times, as might be expected. Gases then diffuse in the inverse ratio of the square roots of their densities.

To these three laws involving the gases, *Avogadro's hypothesis* may be added and our conception of the molecules and their motion will be reasonably complete. This hypothesis is that, in equal volumes of all gases under similar conditions, the number of molecules is the same. This is not capable of absolute proof, but it is supported by much evidence both physical and chemical. As an example of the latter is this fact: When hydrogen and

chlorine unite, exactly one volume of hydrogen unites with one volume of chlorine, and they form together two volumes of hydrochloric acid. There could not be this equality, assuming our chemical theory to be sound, unless the numbers of molecules were the same in each of the three gases. The reaction requires an equal number of molecules per c. c. for each substance.

The equality of the numbers of molecules in equal volumes of gases under similar conditions makes it possible to use a simple device, called the *gram-molecular volume,* in dealing with them. We take the molecular weight in grams for all gases, for hydrogen, 2 g. (the molecule of hydrogen contains two atoms) for oxygen, 32, for carbon dioxide, CO_2,44g. These weights indicate equal numbers of molecules. Upon trial, it is found that 2 g. hydrogen occupy 22.4 liters. Experiment further shows that the gram-molecular weight of all gases occupies this same volume, a fact which must follow also from theoretical considerations. The practical convenience of this agreement is that it makes it an easy matter to establish the relation between molecular weights of gases and their actual weights. To find the molecular weight of a gas it is only necessary to find the weight of 22.4 liters of the gas in grams. The number thus found is the molecular weight. On the other hand, given the molecular weight of a gas, it tells us at once how many grams there are in the gram-molecular volume, 22.4 liters. From this the weight of any desired volume may be calculated.

Now all our laws and hypotheses conform to the facts of mechanics. The pressure of all gases must be equal, for pressure is made up of the individual momentum of all the molecules. Those molecules

which lack in speed compensate for this by the greater weight of the molecule, so that the momentum of all is equalized.

LAWS INVOLVING THE ATOM

The preceding discussion has been one of physics, very intimately associated, however, with chemical discussions. Certain chemical regularities also are observed and these are expressed in laws. These principles have led to the development of the atomic theory. We will assume the latter as fully accepted, and show how it conforms to these laws.

a. Matter is indestructible, for the atom never changes. The atom may unite with other atoms, and separate from them, but its existence as an atom is always maintained.

b. The law of constancy of composition must follow from the constant nature of the atom. The molecule of the compound cannot vary, for it is always built up from the same number of unvarying atoms.

c. The law of multiple proportions is illustrated by the following pairs of compounds, H_2O and H_2O_2, CO and CO_2, SO_2 and SO_3. These compounds, involving the same elements, must be made up in such simple ways, for the atom is the building unit. Carbon united with oxygen may form carbon monoxide, CO, or carbon dioxide CO_2, perhaps other similar compounds, but there can be no variation in proportions, except by simple whole numbers.

Assuming the atomic structure and the atomic weights, these and other laws involving the atom seem self-evident. Historically the development was in the reverse direction. These laws and truths led to the atomic theory.

SOLUTIONS

Solution is generally assumed to be the merging of a substance in a liquid, so that the two form a homogeneous mixture, one that is altogether clear and even throughout. Gases mingle with other gases, they are absorbed by solids, and solids mix evenly as in the alloys. These are all properly solutions, but our chief interest centers in solutions in liquids, and especially in solutions in water.

The *solvent action of water* varies *in respect to gases.* Oxygen and nitrogen (air) dissolve so little that the ordinary observer must have his attention called to the fact of their solubility. 1,000 cubic centimeters of water absorb in all about 20 cubic centimeters of air, of which one-third is oxygen. This is a small amount, yet enough to provide water-breathing animals with oxygen, and to supply enough oxygen for the purification of waters not too highly polluted. Another class of gases includes carbon dioxide, hydrogen sulphide, and chlorine. Water dissolves about equal volumes of each of these, so that the presence of the gases is noticeable by taste, color, and odor. These solutions can even be used for laboratory reagents, but they are very dilute. The volume of the gas, equal to that of the water, represents only a small fraction, about 1/100, of its weight. A third class of gases is represented by ammonia and hydrochloric acid, which are so soluble that in their solutions the water is usually forgotten. One volume of water dissolves several hundred volumes of these gases, from 25—60 per cent by weight, and these solutions show very marked chemical properties.

The solvent action of water on liquids.—There are rather few common inorganic liquids. The three

acids, sulphuric, nitric, and phosphoric, are soluble in all proportions. Among organic liquids, of which there are many, the solubility is usually determined by the presence of the hydroxyl group (OH). Alcohols and organic acids, as acetic and citric, contain this group and are therefore likely to be soluble. Mineral and vegetable oils are insoluble.

The greatest interest attaches to the *solvent action of water on solids.* The matter is usually looked upon from the other side, namely the solubility of solids in water. Their solubility varies considerably, from that of quartz, which is considered to be absolutely insoluble, to that of sodium iodide, which dissolves in less than its own weight of water.

The solubility of solids has in every case an upper limit. For a given temperature the maximum amount which will go into solution is fixed, but the amount varies with the temperature. Below this maximum the solid and water mingle freely.

HEAT AND SOLVENT ACTION

The general effect of heat is the increase of molecular activity. The solution of a solid involves greater molecular activity, so that it is but natural that the effect of heat is to increase the solvent action of water upon solids. For the same reason heat diminishes the solvent action of water upon gases. To dissolve a solid we heat our solvent, to dissolve a gas we cool it; in both cases we strive to attain the liquid state.

Solids dissolved in water exert some influence on the physical properties of the water. It no longer boils so easily, nor does it freeze so easily. The most interesting feature of these facts is that their influence is a regular one, depending upon the actual

number of molecules of the solid present, and not upon its individual nature. Therefore, amounts of solids which show equal numbers of molecules will have the same influence. To obtain molecular equality we need only to apply the molecular weights of different substances in grams, obtained by adding together the atomic weights of the constituent elements. Such weights must contain equal numbers of molecules. Osmotic pressure is the pressure which a solid exhibits in distributing itself through a solvent, and resembles the diffusive power of gases as they distribute themselves through space. In all these respects the solid distributed through a solvent resembles a gas, its conduct being determined by the number of molecules present, rather than by the chemical nature of the molecules.

SUPERSATURATION

When solutions saturated at high temperatures are cooled, we may expect the solute (the substance dissolved) to crystallize out as its solubility becomes lessened by the lower temperature. With care, however, in many cases, the substance may be prevented from separating out, although it is present in amounts above the solubility limit. This is, however, not a condition of equilibrium, and if a crystal of the solute is introduced the excess crystallizes out with great rapidity. This "super" condition applies also to conversion of a gas to a liquid, a liquid to a solid, and a liquid to gas. The change of state is suspended until the equilibrium is established by some outside influence. Water vapor, as it cools, needs solid nuclei to condense on. Water can be cooled below its freezing point, but when agitated in this condition changes suddenly into ice.

CHAPTER XIII

ACIDS, BASES, AND SALTS. THE IONIC THEORY

NO classes of substances are of greater importance than these three. They have been referred to repeatedly and now must be discussed more fully.

Acids invariably contain hydrogen, and under favorable conditions this hydrogen is replaceable by a metal. In such cases salts are formed. Acids may be solids, as boric acid; liquids, as sulphuric acid; or gases, as hydrochloric acid. In the popular mind acids are associated with the liquid condition, and when used in this condition in solution in water, their reactions are most typical.

They have a strong sour taste, and are readily detected by certain colored substances called indicators. Of these litmus is the most common. This last is colored red by acids, it is turned blue by bases, and is not affected by the typical salts. Other indicators show other color changes, but, except for a greater delicacy of action, they have virtually the same application.

Acids fall into two classes, those of the type of hydrochloric acid, HCl. These are the hydro-acids. HCl, HBr, HI and H_2S are the chief members of this group. The acids of the other group contain oxygen and are uniformly built up on the plan of

sulphuric acid, namely a nonmetallic oxide united with water.

Sulphuric acid, $H_2SO_4 = SO_3 + H_2O$
Sulphurous acid, $H_2SO_3 = SO_2 + H_2O$
Nitric acid, $2HNO_3 = N_2O_5 + H_2O$
Nitrous acid, $2HNO_2 = N_2O_3 + H_2O$
Carbonic acid, $H_2CO_3 = CO_2 + H_2O$
Phosphoric acid, $2H_3PO_4 = P_2O_5 + 3H_2O$

Acids vary greatly in strength. Hydrochloric, nitric, and sulphuric are among the strongest, while carbonic acid is exceedingly weak. They vary in stability. Phosphoric acid is decomposed with great difficulty, while carbonic acid separates into its constituents as rapidly as it is formed.

Bases are formed by the union of the oxides of the metals with water. In cases of the more active metals the union is readily accomplished, in others it must be brought about indirectly. The bases are thus hydroxides and in their reactions the hydroxyl group—OH, is likely to remain intact, passing unchanged from one combination to another.

Bases are the complements of acids. They are derived from the metals, the acids from the nonmetals. Bases yield the hydroxyl group, acids yield hydrogen, which together form water, a characteristic by-product of their interaction. Bases turn litmus blue, while acids turn it red. The active bases are corrosive like the active acids, but, when the two unite, they lose their characteristic properties, and the resulting salts are neutral. Bases are solids and only the more active are soluble in water.

Salts are formed by the interaction of bases and acids; water is formed in every case as the by-product.

Salts are usually crystalline substances. Some have a simple salty taste, but many vary from this. Lead salts are sweet, aluminium salts are astringent. Salts are colored only when they contain certain metals or acids. When made up of bases and acids of equal activity, they are neutral substances, as Na_2SO_4, sodium sulphate. If the base is an active one, and the acid weak, the properties of the base predominate, as shown by their turning litmus blue. If however, the acid is an active one and the base weak, the acid characteristics predominate, and such salts turn litmus red. Sodium carbonate, Na_2CO_3 and ferrous sulphate, $FeSO_4$, are such salts. The acids, nitric acid, HNO_3, sulphuric acid, H_2SO_4, and phosphoric acid, H_3PO_4, differ in the amount of the characteristic acid hydrogen which they contain. This shows itself in the possibilities developed when this hydrogen is replaced by a metal. Let sodium be selected for the metal. In the case of nitric acid, the salt formed by replacing the hydrogen by the sodium is sodium nitrate, $NaNO_3$, and there is no other salt possible. When, however, sulphuric acid is the acid in question we may form $NaHSO_4$, sodium hydrogen sulphate, and Na_2SO_4, sodium sulphate, the normal salt. The salts which still contain acid hydrogen are called acid salts, and have the properties of both acid and salt. For this reason they often have unique value.

Salts are formed most simply by the reaction called neutralization, the union between a base and an acid. These reactions proceed with rapidity and completeness. The base supplies the metallic part, the acid the nonmetallic part. The by-product is water, the hydroxyl group coming from the base,

the hydrogen from the acid. Equations showing neutralization differ only in the numbers of groups applied. In all cases the number of hydroxyl groups of the base must balance the number of hydrogens of the acid.

Although neutralization is the simplest way of forming a salt, salts are formed in general whenever a metal replaces the hydrogen of an acid directly or indirectly. Salts may also be considered independently from the acids from which they are derived. It is evident that they must be made up of a metallic residue and a nonmetallic residue. Such salts as FeI_2, ferrous iodide, and FeS, ferrous sulphide, are simply made up of the metal and the nonmetal, and they are prepared by the simple union of these. Salts containing oxygen are more complex, but their composition may readily be appreciated.

Calcium carbonate, $CaCO_3 = CaO + CO_2$
Calcium sulphate, $CaSO_4 = CaO + SO_3$
Sodium sulphite, $Na_2SO_3 = Na_2O + SO_2$
Lead nitrate, $Pb(NO_3)_2 = PbO + N_2O_5$
Calcium silicate, $CaSiO_3 = CaO + SiO_2$

It is not always possible to put together these constituents in order to prepare salts, but the borates and silicates, especially in glass making, are thus prepared. In decomposing salts at high temperatures this aspect of their structure is of prime importance, and they usually decompose in accordance with this idea of their composition.

As acids and bases represent the typical active compounds of inorganic chemistry, so salts represent the end products of many chemical reactions. If we imagine an active base, as sodium hydroxide, somehow formed in the course of nature, its affinities are such that it would unite with the first

substance of acid nature with which it came in contact. The product would be a salt. So also any active nonmetallic substance would sooner or later form an acid, by union with oxygen and water. This acid then would combine with the first substance of basic nature with which it came in contact. Such a course of events takes place in the case of the so-called sulphur found in coal. The sulphur is actually in the form of iron sulphide, FeS_2, which upon burning, or uniting with air, yields sulphur dioxide, SO_2. This unites gradually with more oxygen to form sulphur trioxide, SO_3, which in its turn forms sulphuric acid, H_2SO_4. This acid soon unites with basic substances, especially calcium and magnesium compounds, and forms salts, sulphates, in which form it is likely to remain indefinitely. The great mass of the earth's crust is composed of compounds of the order of salts, in which the affinities of the elements and compounds have spent themselves. Active substances like free sulphur and boric acid are found occasionally, but they have been formed under unusual conditions and have been protected by chance from the normal reactions to which they are subject.

MOLAR SOLUTIONS

In discussing chemical reactions, it is evident that the units of all reactions are atoms and molecules. If we combine calcium oxide, CaO, and sulphuric acid, H_2SO_4, one molecule of each is needed. We cannot of course pick out one molecule, but if we take the molecular weight of each, in grams, respectively 56 grams and 98 grams, we will have equivalent amounts, representing the same number of molecules for each. This is the principle of molar

solutions. Molar solutions are made by dissolving the gram-molecular weight of any substance in one liter of water. Any given amount of such a solution will correspond exactly to the same amount of any other molar solution.

NORMAL SOLUTIONS

Molar solutions are only partially satisfactory. One molecule of sulphuric acid, H_2SO_4, will require two molecules of sodium hydroxide, NaOH, to neutralize it, and phosphoric acid, H_3PO_4, containing three hydrogen atoms, requires three molecules of sodium hydroxide. It is a convenient expedient, therefore, to reduce all solutions to the simplest possible equivalent. If molar sulphuric acid is diluted to half strength it will now just balance the molar sodium hydroxide solution. So phosphoric acid, H_3PO_4, must be reduced to one-third strength. Calcium hydroxide, $Ca(OH)_2$, must be reduced to one-half strength, and so on. Such solutions, reduced to an absolute equivalence, are called normal solutions, and form the basis of all fine chemical work involving solutions.

It will not be difficult to appreciate that normal solutions may be too concentrated. Normal sodium hydroxide contains 40 grams in one liter. Normal sulphuric acid, 49 grams. Hence normal solutions are usually diluted and used as half normal, fifth, tenth, or twentieth normal, to suit the convenience of the operator. The exact relationship between different solutions of course still continues to apply.

IONIZATION

The reactions which involve solutions of acids, bases, and salts take place with a degree of readiness

and completeness which differentiate them from all others. Sodium has a striking affinity for chlorine, and their compound, sodium chloride (salt), NaCl, is exceedingly stable and can be decomposed only with great difficulty. But if a solution of sodium chloride is treated with one of silver nitrate, the chlorine is found to combine with the silver instantly.

Potassium hydroxide reacts at once and completely with an acid, and also with many salts. Instances of reactions of these types can be found in great numbers. All such reactions are explained with great clearness by the assumption of the ionic hypothesis. Briefly stated this is as follows.

When acids, bases, and salts are dissolved in water, they dissociate into their constituent groups, hydrogen or metallic on the one hand, and hydroxyl or nonmetallic on the other. These groups are distinguished from other groups or atoms by carrying a positive or a negative charge of electricity and are called ions. Being dissociated as soon as placed in solution, they are ready to react as soon as they meet with other groups with which reaction is possible. This dissociation is called ionization.

I. Ionization applies to acids, bases, and salts only. Even then only the stronger acids and bases are ionized to any considerable degree, and the lack of ionization of the weaker bases and acids gives rise to various phenomena, especially to an important action called hydrolysis. It is safe to assume that all salts ionize.

II. The substances must be in solution in water. This is readily illustrated by dissolving hydrochloric acid gas in benzene. It then fails to respond to the

tests which are usually applied to acids. Other reagents probably ionize substances dissolved in them, but compared with water their importance is insignificant.

III. Dissociation differs from decomposition in that in the former case the separated parts readily reunite, as soon as the conditions which have caused their separation are modified. If we heat ammonium nitrite, NH_4NO_2, it decomposes into water and nitrogen, $NH_4NO_2 \rightarrow 2H_2O + 2N$, and only elaborate roundabout methods will serve to unite them to form the original substance. This is decomposition. When however ammonium hydroxide, NH_4OH, is gently heated, the separation into its parts may be reversed by mere cooling of the residual water, $NH_4 \rightleftarrows NH_3 + HOH$. This then is a dissociation. In the process of separation into ions we have a case of dissociation. $Na\,Cl \rightleftarrows Na^+ + Cl^-$. If more water is added, the dissociation is increased. If water is allowed to evaporate, the ions reunite to form the original salt. The degree of ionization may be increased or decreased by simply varying the amount of water present.

IV. The ions are the groups, composed of one or more atoms, which preserve their individuality through many reactions. They are positively or negatively charged as will be shown in the sequel, and it is these charges which differentiate them from the original atom or atoms. In any complete compound, the number of positive charges upon the positive ions, must equal the number of negative charges upon the negative ions. The sum total then of the charges for any molecule is zero, the charges balancing each other when the molecules are reformed. SO_4 is a common negative ion, but with-

out its charges it cannot exist. If we discharge it electrically, by bringing it in contact with the positive pole of a battery, it at once decomposes into sulphur trioxide and oxygen, $SO_3 + O$. The groups which form ions are readily learned from a consideration of acids, bases and salts. The positively charged ions are hydrogen and the metals. The negatively charged ions are either hydroxyl or the nonmetallic groups.

Various elements or groups carry more than one charge, either positive or negative, according to their valence. The total number of positive charges balances the total number of negative charges. Acids, bases, and salts are called ionogens, a name indicating that they are capable of producing ions when dissolved in water.

The peculiar properties of acids and bases are due to the reactive hydrogen and hydroxyl ions respectively. Hence their strength is determined by the amount of ionization which takes place when they are dissolved in water. A strong acid or base is one that is highly dissociated, a weak acid or base is only slightly dissociated. The conductivity for electricity is also determined by the number of ions present. The values found for strength of acids and bases, and that found for their conductivity are found to be the same.

In accordance with this ionization hypothesis, acids, bases, and salts may be defined again in new terms. Acids are compounds which yield positive hydrogen ions when dissolved in water. The other ion is perforce negative and can be composed only of a nonmetallic group. Bases are compounds which yield negative hydroxyl ions; the other ion is of course positive and must be composed of a metal. A

salt yields positive metal ions, and negative non-metal ions.

Water itself is very little ionized. In comparison with the more active bases, acids, and salts its ionization may be considered negligible. But when very weak bases and acids come into consideration, the very slight ionization of water must be considered.

The evidence of the ionization hypothesis is drawn from various considerations based upon physical measurements of solutions. Solutions containing ionogens show abnormal characteristics in respect to their freezing points, boiling points, and osmotic pressure. Solutions of sodium chloride, NaCl, for example, shows an effect which would be due not to the presence of one molecule, but of two. This is to be attributed to the fact that in aqueous solution this salt yields, not one molecule of NaCl, but two units, namely, Na^+ and Cl^-. Electrical measurements are in agreement with this. There are indications of ionization outside the field of these delicate measurements. The ready reactivity of ionogens is such an illustration. Solutions of ionogens conduct electricity, for the current is carried by the ions, and electrolysis is another illustration. The colors of salts in solution often show ionization. Copper sulphate by itself is white, copper chloride is yellow, copper bromide is olive colored, yet, when they are in solution, they all show the blue color of the common copper ion.

ELECTROLYSIS

This is one of the fascinating chapters of chemistry. Its details are explained with ease by means of the ionic hypothesis. This assumes that when an ionogen (acid, base, or salt) is dissolved in water,

it is dissociated into ions, certain of the ions carrying positive, and others negative charges. So far, the electric current has not come into the discussion. Let us place the two poles of a battery into a solution of an ionogen. The negative ions of the solution will now begin to travel toward the positive pole, and the positive ions to the negative pole. This conduct has given origin to the name ion, which means to move or to travel. When the ions have arrived at the corresponding pole, the positive charge of the pole and the negative charge of the ions neutralize each other and the ion ceases to exist as such. The same happens at the negative pole. Hence at these two poles we have released atoms or groups of atoms, no longer in the ionic form. This will be best understood by following specific illustrations.

A. We take a solution of copper chloride, Cu^{++} and $2Cl^{-}$, and introduce the poles of a battery. The copper ion is drawn to the negative pole and its charge is neutralized. The Cu^{++} ion has now become ordinary copper, Cu, and is deposited on the pole. So the Cl^{-} ion is converted into chlorine, Cl, and escapes as the familiar gas.

Electrolysis is supposed to be the separation of a compound into its parts by means of electricity. It will be seen that the separation was already affected by the ionization, and that the current merely discharged the ions previously present.

B. To illustrate another phase of electrolysis we select sodium chloride, $Na^{+} + Cl^{-}$. After the current is passed we will have sodium atoms, not ions, at the one pole, and chlorine at the other. Sodium being in the presence of water, will react with the oxygen of the water and form sodium hy-

droxide, and hydrogen will be liberated. The original action is the same as with the copper chloride solution, but a secondary reaction takes place on account of the activity of the sodium. The chlorine escapes as before.

C. Copper sulphate shows another form of secondary reaction. The electrolysis develops Cu, the metal, which is deposited, and SO_4, a hypothetical group, which can exist only as part of a compound or as an ion. It then must break down into substances capable of existence by themselves. Such are SO_3 and O. Hence at the positive pole oxygen will be evolved, and the residual sulphur trioxide will form sulphuric acid with the water present.

D. Sodium sulphate, Na_2SO_4, illustrates the most complicated case. As the result of electrolysis we should have Na_2, sodium, and SO_4, sulphate. The former, however, reacting with water yields sodium hydroxide and hydrogen, NaOH+H, the latter hydrogen sulphate and oxygen, $H_2SO_4 + O$.

These four cases represent essentially all the ordinary complications of electrolysis. On account of the response of acids, bases and salts to the action of electricity, they are often called electrolytes. Ionogen and electrolyte are terms applied equally correctly to these substances, although they may lay emphasis upon different phases of their conduct.

The applications of the principles of electro-chemistry to batteries, electro-plating and similar problems will be discussed more advantageously under the head of the metals.

CHAPTER XIV

THE METALS, OR BASE-FORMING ELEMENTS

THE rough classification of all the elements into two groups, metals and nonmetals, is based upon essential differences in both physical and chemical respects. Metals as a class, considering the well known metals, are opaque solids, heavy, malleable, that is, they can be flattened out under the blows of a hammer, good conductors of heat and electricity, mostly of a silver color, and possessing a shine which is called the luster. The nonmetals on the other hand are not predominantly in any one of the three physical states. They vary much in weight, are brittle, nonconductors, have a variety of colors, and no marked luster. The chemical differences are even more pronounced. The metals form bases, the nonmetals acids. In salts the metal is positive, the nonmetal negative. Some metals have less pronounced characteristics, and a number of elements are doubtful, but in the main the classification is logical and useful.

The popular impression as to what constitutes a metal is correct as far as it goes, but it includes in its range only one type of metals, those which are in ordinary use. In this group are platinum, gold, silver, mercury, copper, lead, tin, nickel, iron, zinc and aluminium. These metals are of such low chemical activity that when they are once obtained free,

they are permanent enough to serve many purposes. These purposes are mainly based upon the physical properties of these metals, such as tensile strength, ductility, malleability, toughness, great weight, conductivity for electricity, color, and luster. To this group we are now ready to add another group of metals, sodium, potassium, calcium, magnesium, and several others. These differ mainly in two respects. They are light, only one being as heavy even as aluminum, and they are so active chemically that they are obtained free with great difficulty, and readily revert to compounds. It is in the form of compounds that they are useful, while the first class mentioned finds its usefulness in the form of the element. The designation of light and heavy metals is a very suggestive one, although the demarcation of properties is not absolutely sharp. It is interesting that the present generation has seen aluminum taken out of the class of metals used only in the compound form, and placed in the class, so far as usefulness goes, of the heavy metals. The advantage of such a metal is great. The next generation may see this same proceeding in the case of magnesium. This metal is so unfamiliar that the word is known only as applied to compounds, yet automobile pistons are being manufactured from magnesium, and its use is likely to be much extended.

THE ELECTROMOTIVE SERIES

Barring the points of difference just discussed, the metals may be said to be strikingly alike in their chemical properties. This resemblance applies to the nature of their affinities; but in respect to the intensity of their affinities, they vary greatly, from the highly reactive potassium, to inactive gold, which

forms compounds only with difficulty. If the intensity of the affinities among all the metals is compared, they may be arranged in order, the most active first, the least active last. This list is called the electromotive series, and may be used in many ways as the index of the chemical properties of the metals.

THE ELECTROMOTIVE SERIES

Cæsium	Aluminium	Hydrogen
Rubidium	Manganese	Arsenic
Potassium	Zinc	Copper
Sodium	Chromium	Antimony
Lithium	Iron	Bismuth
Barium	Cobalt	Mercury
Strontium	Nickel	Silver
Calcium	Tin	Platinum
Magnesium	Lead	Gold

Each metal of this list has a greater tendency to go into combination than any following it, and a lesser tendency than any preceding it. If, therefore, we introduce zinc into a solution of copper sulphate, the zinc will go into solution, forming zinc sulphate, and the copper will be deposited. Hydrogen is included, as it takes the place in acids, which the metals take in salts. All the metals mentioned in the first two columns will directly displace the hydrogen from acids. Those in the last column will do so only indirectly. A practical outcome of this relation of hydrogen is that only these last metals are found free in nature, while all metals preceding hydrogen are found only in compounds. The metals mentioned in the first column are the more active metals known mostly in their compounds.

We may summarize. In the electromotive list we have a complete arrangement of the metals in respect to the intensity of their affinity. These

may be roughly divided into three groups represented by the three columns: A, the most active, known and used mostly in the form of compounds, ending with magnesium; B, the more active of the common metals ending with lead; C, the less active of the common metals, the last three being known as the noble metals on account of their low chemical activity.

OCCURRENCE OF THE METALS

The study of the earth's crust impresses us with the preponderance of two nonmetals, oxygen and silicon; and of six metals, aluminium, iron, calcium, magnesium, sodium, and potassium. All the other metals are present in insignificant amounts compared with the whole mass of the earth. When we look for them in ordinary rock they are difficult to find. It is only through concentrations of scattered masses, and through concentrations of concentrations, that such metals as lead, copper and zinc are found in amounts sufficient to be useful. Fortunately there are such concentrations, and men seek for them and utilize them with the greatest eagerness.

For any general discussions it is expedient to consider the metals in the two groups; the more active metals, ending with magnesium, and the less active metals, including the rest. The more active metals are found in nature only in compounds in two general states. The first of these is as a constituent of the primary rock of the earth, in the form of more or less complex silicates. They are in these forms in stable combination and are practically unavailable to men. The second set of compounds represent decomposition products of the first,

formed through endless years of weathering and other agencies, and subsequent concentration in forms which are ordinarily of great usefulness. Common salt and the German potash deposits are of this order, while the vast quantities of potassium compounds tied up in the mineral feldspar are altogether useless in the present state of the chemical industries. The ocean represents a concentration of compounds of sodium and other metals, while the many salt deposits of the land represent a still further concentration, with an increased advantage to men.

The metals of the active group are useful mainly in the form of compounds. Sodium, potassium, calcium, and magnesium form many such compounds which are applied in various ways. In the study of these metals, then, the elements play a minor rôle. Compounds of metals are in the form of oxides, hydroxides, and the salts, of which the most important are carbonates, chlorides, sulphates and nitrates. Some other salts also come into consideration, like the phosphates of sodium and calcium.

The less active metals occur in somewhat different forms in nature. Aluminium and iron are abundant in the form of silicates, in primary rock, but the useful compounds of these and other metals are found in secondary formations and concentrations. Among these utilizable forms are the oxides, as iron oxide, Fe_2O_3, the hydroxides, as limonite, iron hydroxide, $Fe_4O_3(OH)_6$, the carbonates, as zinc carbonate, $ZnCO_3$, and the sulphides, as lead sulphide, PbS. Chlorides and sulphates do occur, but in lesser abundance. The least active metals mentioned near the end of the electromotive list occur

in the free state. The chief in this group are copper, bismuth, platinum, and gold.

As these elements are of use chiefly in the free form, as metals, the extraction from their ores is a most important chemical consideration. This will be described in a later chapter on metallurgy. It may here be outlined most briefly. The extraction of the metals takes three main forms. The first is treatment of the oxide, and this includes hydroxide and carbonate, for, upon heating, these are converted into the oxide. The oxide is simply heated with carbon, which combines with the oxygen, and the metal is left free.

When an ore is in the form of sulphide it must first be converted into the oxide by "roasting," that is, heating in a current of air. The sulphur is thus disposed of and the metal oxide is now ready for reduction by means of carbon.

The third type of ores includes those which contain the metal in the free form. The metal may simply be melted out. But in the case of gold and platinum the metal is so thinly scattered that various devices must be applied. Some of these devices are of chemical nature, as conversion of the gold into chlorides and cyanides and washing out the soluble salts, from which the gold is readily recovered. They may also be physical, as the process of amalgamation, that is, solution in mercury, or separating the heavy particles of gold from the lighter particles of rock by flushing with water.

CHAPTER XV

THE ALKALI METALS

THE whole class of metals will be considered in four groups, departing somewhat from the usual classification. The first group will consist of the alkali metals, the first five of the electromotive list. The next group will include the group of alkaline earth metals, the next four of the list. Our third group will include the less active metals, down to hydrogen, and the last group the remainder. The numerical balance is by no means maintained by this classification, but the chemical ideas are better developed.

The alkali metals include five closely related metals.

	Atomic Weight
Cæsium, Cs	133
Rubidium, Rb	85.5
Potassium, K	39.1
Sodium, Na	23
Lithium, Li	7

The first point in their relationship is the difference in their atomic weights. Among similar elements the difference between the lower atomic weights is always found to be 16; and this is the difference found between the weights of the lighter metals in the list above. The next difference is about 45, as in the chlorine group, and this applies to the other two intervals among the alkali metals.

In the case of the chlorine group, the more active and characteristically nonmetallic element is that with the lower atomic weight. Among the metals the reverse is true, and cæsium, with the highest atomic weight, is the most active. These five metals are remarkably alike. They have the same valence, 1, they occur in similar manner, the metals are active, oxidizing spontaneously in the air, so that they must be kept under an oil free from oxygen. They burn when heated and decompose water readily. Their hydroxides are very soluble and strongly basic, and their compounds are in the main stable and soluble. They impart characteristic colors to the Bunsen flame, and give simple lines in the spectroscope. These properties are all markedly different from those of other metals. After the resemblances among these metals have been established, our attention is attracted to their differences. These are in degree, and not in kind. For example, potassium decomposes water with energy sufficient to cause the liberated hydrogen to ignite. Sodium causes the ignition of the liberated hydrogen only under favorable conditions. Lithium develops much less heat. The flame colors and the spectra are characteristic for each metal, so that, if the compound is pure, the metal may readily be recognized. By other tests it is very difficult to distinguish between them, for they respond very similarly to most reagents.

SODIUM

Sodium is the most important metal of the group. It exceeds potassium in this respect mainly because it is more available. The natural concentrations of sodium compounds are so much greater than those of potassium that the industries turn to the former

wherever it is possible. Plants require potassium, and sodium cannot therefore be substituted in fertilizers. Otherwise there is an increasing tendency to turn to sodium for all applications of an alkali metal.

Sodium is a bright white metal; on account of its chemical activity it tarnishes instantly on exposure to air, hence its luster is unfamiliar. It is lighter than water and so soft that it can be molded easily. Chemically, it is characterized by a great affinity for oxygen, so that it must be kept under oil; it oxidizes spontaneously, burns readily, and decomposes water with the liberation of hydrogen.

When sodium burns, or one of its compounds comes in contact with a flame, the flame is colored yellow, a characteristic of sodium. In general, sodium unites readily with nonmetals, especially with the halogens.

When sodium burns, the compound normally to be expected would be sodium oxide, Na_2O. There is formed instead *sodium peroxide*, Na_2O_2, containing an excess of oxygen. This excess of oxygen, coupled with the great activity of the oxide, makes sodium peroxide a powerful oxidizing agent. As hydrogen peroxide is readily prepared from it, it is used indirectly for bleaching.

SODIUM HYDROXIDE

This is the typical base of chemistry, as sulphuric acid is the typical acid. It is a white, that is, colorless, solid, exceedingly soluble in water. Its solutions have a characteristic slippery feel. Chemically it is characterized by strong basic reactions. It neutralizes acids with great readiness. It is so powerful a base that it will extract from the at-

mosphere and combine with the exceedingly weak acid, carbonic acid, formed by the union of carbon dioxide with water. Its greatest use is in the making of soap. It is used for removing fatty material from textiles, for mercerizing cotton, and wherever an active base is needed for furthering chemical reactions and neutralizing acids. In purely scientific operations it is used in endless ways, depending in the main on its strongly basic properties.

SODIUM CARBONATE

Sodium carbonate is made and used in vast quantities. As the dry salt it is called soda ash and is used much in the industries. Its use depends on three principles. It carries the carbonate group, and hence is used in water softening to convert soluble calcium compounds into insoluble calcium carbonate. It is a mildly alkaline substance. The active sodium base is only partly neutralized by the weak carbonic acid, so that it has cleansing properties in respect to fatty substances. It is used in laundries and in cleansing powders, and is known to be rather corrosive. Finally it is a convenient raw material for making most of the other sodium compounds which the industries demand. Illustrations, sodium hydroxide and glass.

In the household it is known as sal soda, or washing soda, and is applied in the form of its crystallized salt. This form is more conveniently handled. Its use depends upon the second of the principles mentioned above.

SODIUM HYDROGEN CARBONATE

This salt is the common baking soda. Its formula is $NaHCO_3$, which indicates that it is carbonic acid

H_2CO_3, with one hydrogen replaced by sodium. Another way of considering it is as sodium carbonate added to carbonic acid. This last aspect has resulted in the name sodium bicarbonate, it being considered as sodium with a double portion of carbonate. Because of this double portion of acid, the strongly basic properties of the sodium are pretty well neutralized, and the salt is a mild, nearly neutral substance, suitable for use in foods, where it serves as a source of carbon dioxide for leavening, and is of service in neutralizing acids which may be undesirable.

Baking powders are used in large quantities to supply a gas for the purpose of lightening dough and batter. Air is often beaten into dough, and steam is at times the leavening agent, but the most convenient gas is carbon dioxide, CO_2, and its most convenient source is baking soda. In order to liberate the carbon dioxide the sodium of the soda must be replaced by hydrogen. Any acid will supply this hydrogen, but few acids are tolerable in connection with foods. The most familiar substances used are tartaric acid and its acid salt cream of tartar. Another source of hydrogen is calcium or sodium hydrogen phosphate, which is more readily available than the cream of tartar. These substances are mixed in the dry form, and enough starch added to keep them from interacting until they are used.

The residue which these powders leave in the food is considerable. One pound of cream of tartar baking powder leaves almost three quarters of a pound of Rochelle salts. But no effect has ever been traced to this in the food. The phosphates formed in the phosphate baking powders might be considered of value, but, as in other powders, no result is noticeable.

Alum baking powders are not altogether popular, yet they are used, and the reaction involved is of interest to the chemist. Alum is used as a substitute for the more expensive phosphate and tartrate. Such baking powders are made up of aluminium sulphate and baking soda. When used, the combination forms aluminium carbonate tentatively. This is a compound of a weak base and a weak acid and at once breaks up, yielding the carbon dioxide.

Another form of baking powder, which is interesting, but almost unheard of in this generation, is ammonium carbonate. No further ingredient is needed, as the heat of the oven decomposes it into carbon dioxide, ammonia, and water. There is no residue.

SODIUM SULPHATE

Na_2SO_4, dry, or $Na_2SO_4.10H_2O$, crystallized. This is a by-product formed in large quantities when sodium salts are treated with sulphuric acid. Its greatest use is for glass making, in which operation only the sodium oxide contained therein is used. The rest is wasted. Sodium hydrogen sulphate, $NaHSO_4$, is a typical acid salt. It has a limited use as being both acid and salt.

SODIUM NITRATE, $NaNO_3$

This salt, because of its relation to nitric acid, is one of the most important raw materials of chemistry. Its occurrence in nature in such large quantities as those found in South America is a matter of surprise, because soluble compounds of nitrogen are seldom abundant. Besides being the raw material for nitric acid, it is valuable as a fertilizer on account of its nitrogen content. It is used to a limited extent for making blasting

powders, but absorbs moisture too readily to be universally applied. Before the sodium nitrate deposits were available, potassium nitrate served its purposes. In these days the amount of potassium nitrate which could be produced would be altogether inadequate.

SODIUM CHLORIDE, NaCl

Common salt is almost in a group with water and sulphuric acid as being the substances which count for most in the chemical world. Its interest lies in its form of occurrence, accumulated in such vast amounts in the sea, its need in the food of men and animals, and its being the source of all the sodium compounds and the chlorine which men use.

As the solid rocks of the earth's crust disintegrate their physical breakdown is followed by chemical decomposition; and compounds of sodium, potassium, calcium, and magnesium pass into solution. Potassium compounds are to some extent retained by the soil and later taken up by plants, and calcium and magnesium carbonate too are probably deposited. But considerable amounts of all four reach the sea and are accumulated there. Of these four sodium is predominant and it has, for reasons which are not clear, taken the form of sodium chloride or common salt. It is safe to say that the salts of the sea are the final products formed after all possible changes of these compounds have worked themselves out. The sea contains about 3.5 per cent salts, of which about four-fifths is common salt.

The amount of salt in the sea, when considered from the standpoint of human interests is enormous. When compared with the great mass of the earth's crust it is less imposing, as it comprises only about

0.3 per cent of the whole. Sea water varies somewhat, especially in land-locked seas, where there is an influx of fresh water or unusual evaporation. The waters of the Black Sea and of the Baltic Sea are much less salt than those of the ocean, whereas the Red Sea contains an excess of salt.

Salt content of various waters.

Atlantic Ocean	3.5 per cent	
Indian Ocean	3.6 "	
Red Sea	5.0 "	and above
Mediterranean Sea	3.9 "	
Baltic Sea	1.2 "	and less
Black Sea	1.8-2.2 "	
Lake Erie	.001 "	
Mississippi River	.002 "	

The accumulation of salts is not confined to the ocean. The salt lakes are similarly reservoirs of accumulating salts. There are many of these in Asia and Africa. But the three following are best known:

Dead Sea	23 per cent	salts
Caspian Sea	1.3 "	"
Great Salt Lake	19 "	"

In these lakes and many others, sodium chloride predominates, but in some of our western lakes, as well as in many in Africa, sodium carbonate is the final form of the sodium. The alkali deposits which are common in arid regions have an origin similar to that of common salt.

When some arm of the sea has been shut off from the main body of water, and in course of time the water has evaporated, salt deposits are formed. Such deposits should contain all the salts of the sea. However, this is exceptional, as the less abundant salts either escape deposition or are dissolved away

later. These deposits, therefore, are made up mainly of common salt.

Salt is obtained from its natural sources in several ways. Sea water and the waters of the Great Salt Lake are evaporated for the salt. But the greater portion comes from subterraneous deposits, like those in New York and Louisiana. Salt is actually mined in some of these, but the more common method of obtaining it is by forcing fresh water down to the deposits. After it has become saturated the brine is pumped up and evaporated. The process is simple, but there is opportunity for much ingenuity in the economical application of the fuel used for evaporation and the machinery used for handling.

The uses of salt are for food, not alone for kitchen and table use, but also in preparation of such foods as butter and in curing meats. Cattle consume much salt in their food. Salt is the source of most of the sodium compounds used, as also of chlorine and hydrochloric acid. It is applied in silver extraction in the process by which the silver sulphide is first converted to silver chloride, and much is consumed for the purpose of refrigeration.

The list of sodium salts of lesser importance than those already mentioned is a long one. Sodium is such a typical metal that it forms salts with all the acids, strong or weak. The salt is the form in which many elements and groups of elements are applied, and sodium is the most convenient metal for making salts. Among such compounds the following may be mentioned. Sodium sulphite, Na_2SO_3, used for bleaching, as an "antichlor" to remove excess of chlorine and in photography. Sodium thiosulphate, $Na_2S_2O_3$, the "hypo" of the photographers, has some-

what similar uses. Sodium nitrite, $NaNO_2$, is the source of nitrous acid in the preparation of dyestuffs. Sodium phosphate, Na_2HPO_4, is applied in enamels, textiles, and in medicine. Borax, $Na_2B_4O_7$, or sodium borate, is used in glazing, brazing, and as a cleansing agent. Sodium cyanide, NaCN, is gradually displacing potassium cyanide in gold extraction and electroplating. Sodium silicate, $Na_2Si_2O_5$, water glass, is interesting because it is a form of glass, which, on account of its freedom from metals of the next group, is soluble in water. It is used as a preservative, and an adhesive, and is mixed with textiles to make them fireproof.

SOAP

The chemist considers the amount of sulphuric acid manufactured as the index of industrial progress. He might also claim that from the social standpoint the chemical industry of greatest significance is the manufacture of soap. Soap-making is chemically simple. Fats are salts, purely organic, with base and acid like any other salt. The plural word fats is used because there are many of them, all of the same general structure, and differing from the standpoint of soap-making in no essential way. When fat is heated with concentrated sodium hydroxide solution, the strong inorganic base combines with the organic acid to form a sodium salt, which is soap.

The cleansing action of soap carries us into a field called colloidal chemistry. For our present purpose a simple explanation will give us some clue to the fat-removing qualities of soap. It is the removal of fat, either of food, or from the body, which is the great problem of cleansing. Fat is not soluble

in water, it is not even wet by water, facts which might be anticipated from its composition. But water must be the great cleansing agent, and we have in soap a substance which serves as an excellent intermediary between water and fat. Soap is made up of sodium, and the compounds of sodium are soluble and closely associated with water. The other part of soap is the fatty residue, and this end of the molecule establishes contact with the fat. The final effect is that soap water wets the fat, tears off parts of it and in fact emulsifies it, so that it forms tiny droplets which the water is able to wash away. This applies to many other substances as well, such as kerosene, although soap is by no means universal in its action.

Years ago, before sodium hydroxide (lye) was purchasable at every distribution point not too remote from the centers of industry, soap was made from materials available on the farm. The potassium carbonate of wood ashes was leached out and treated with lime. The potassium carbonate was thus converted into the more active potassium hydroxide, and with this the fat was heated. The action is the same as with sodium hydroxide, except that the soap in the end does not harden. Thus the old-fashioned farm soap was soft soap. This custom must be nearly in oblivion, yielding, like so many other home industries, to the more effective competition of the factory.

Concerning the general features of the chemistry of soap, there is not much more to be said. There is little difference in different soaps except in the purity of the ingredients, and in the exactness of the balance between the fat and the lye. For toilet purpurposes the lye should be carefully balanced. For

laundry purposes an excess of lye is an advantage. Ordinary soap contains considerable quantities of water, and when the housewife lets it dry out, she simply causes it to become hard so that in its use it does not waste away so fast. There is an element of fallacy in this, because until the soap is dissolved in water it is of no use.

One complication in the use of soap appears when it is used with hard water. The latter contains small amounts of calcium and magnesium salts in solution. These salts react with the soap as follows: Sodium stearate (soap) + Calcium sulphate → Sodium sulphate + Calcium stearate. It seems that the soap is destroyed, and in its place is formed the insoluble calcium stearate, which serves no purpose as soap, and in fact adds to our troubles, as it forms a disagreeable scum. The softening of water consists simply in removing these calcium or magnesium salts.

POTASSIUM

A description of potassium is a rehearsal of that of sodium with minor modifications. The occurrence of potassium in primary rocks parallels closely that of sodium, there being little difference either in the nature of the minerals or in their amounts. However, as rock disintegrates, sodium compounds find their way to the sea, and potassium compounds are retained by the soil and enter into the constitution of plants. In the sea potassium is only about one-thirtieth as abundant as is sodium. Available sources of potassium, that is, concentrated deposits of secondary potassium compounds derived from the primary rock, are so rare, that when the war interrupted the German supplies, the dearth was acute. Great activity was then manifested in

seeking new sources of supply, with only partial success.

Of the vast amounts of potassium compounds produced from the German deposits in their flourishing years, about seven-eighths was applied to agriculture, and the rest to the potassium industries. As a plant food potassium cannot be replaced by another metal, and there are several other uses to which potassium compounds are peculiarly suited, as the making of soft soap and hard glass. In all probability experiment and experience will demonstrate that in most applications of potassium compounds outside of agriculture, the more available sodium compounds will serve the purpose equally well, and sodium will continue to make inroads in the field hitherto served by potassium.

Potassium itself is obtained less readily than sodium, and there is no occasion for its preparation in more than small amounts. It is noticeably more active than sodium. The most important compounds of potassium are these: hydroxide; carbonate; acid carbonate; chloride; bromide; iodide; nitrate; sulphate; chlorate; cyanide. They are all very similar to the corresponding sodium compounds; but slight differences are to be noted in respect to solubility and conduct toward the moisture of the air. All potassium compounds color a Bunsen flame violet to purple. As stated above, the use of many of these compounds is yielding to that of the corresponding sodium compounds.

Potassium nitrate retains a special interest on account of its connection with black gunpowder and pyrotechnics. Black powder has yielded almost entirely to smokeless powder, and even in black powder sodium and ammonium nitrates are replacing potas-

sium nitrate. Black gunpowder is made up of 75 parts potassium nitrate, 13 parts charcoal, and 12 parts sulphur. These ingredients are thoroughly mixed by long grinding. When ignited, the charcoal and sulphur burn with the greatest readiness, combining with the oxygen of the nitrate. The reaction is so complicated that no single equation can be used correctly. The essential result is that an abundance of highly heated gases is produced. These consist of carbon dioxide, carbon monoxide, and nitrogen, and their sudden formation and expansion cause the explosion. The solid ingredients form potassium carbonate, sulphate, and sulphide, which are blown into the air in the form of smoke. It is this smoke, or solid residue, which has done so much to discredit the use of black powder in warfare. The modern smokeless powders are made up essentially of cellulose nitrate, $C_6H_7O_2(NO_3)_3$, whose ingredients all pass off in the gaseous form, and so produce no smoke.

The explosion of gunpowder is perhaps more correctly termed a rapid combustion. This was initiated in the earliest firearms by igniting the charge through a touchhole by means of any convenient torch. The flintlock was an advance, in that a spark was produced by the flint and steel as occasion required. The percussion cap was a greater step in advance. In this a highly unstable substance, mercury fulminate, was exploded by the blow of the hammer, and the heat of its decomposition set the powder on fire. The modern cartridge simply includes the cap in the cartridge in a much more convenient form. This ignition is different from the detonation used in firing the so-called high explosives.

In making a survey of the uses of compounds of the various metals, several general principles may be observed. The salts are often used for their properties as a whole. Sodium carbonate and borax are useful in cleansing because they have certain desirable properties. The same is true of glass and lead pigments. Secondly, many salts are applied simply for the metal which they contain. Sodium salts used in glass making lose all but the sodium oxide in the fusion. Any potassium compound will serve as a fertilizer, as it is the potassium which is efficient regardless of the rest of the molecule. Copper sulphate and silver nitrate are simply convenient sources of these metals. Thirdly, many salts are used solely for their acid constituent, and the metal is used simply as a means of holding the acid in a convenient form. The metals which are likely to be used for such purposes are sodium, potassium, calcium and magnesium, and of these sodium is the most generally useful. Illustrations are; baking soda, $NaHCO_3$, used for the carbon dioxide to be obtained from it; potassium nitrate and chlorate, used for the oxygen content; sodium sulphite, for the sulphur dioxide, which is a bleacher and an antiseptic; bleaching powder is a convenient form of handling and applying chlorine. The uses of chemical substances run into endless channels, so varied that it is almost impossible to follow them. The principles outlined above, however, are simple and outstanding.

The metals of the sodium group are called the alkali metals. The name alkali is associated with the active hydroxides and carbonates of these metals, but it has been further extended to include the whole aspect of these metals in a broad way. The striking

characteristics of this group may be thus summarized. In the metallic form they are so active that they oxidize spontaneously when exposed to the air, burn readily, and decompose water. Their hydroxides are soluble and exceedingly active, uniting even with the weakest acids. Their carbonates are soluble and mildly alkaline, and the salts as a class are well defined, stable and soluble. Their compounds impart a characteristic color to the Bunsen flame, and in the spectroscope show simple lines.

In a previous chapter, under nitrogen, mention was made of the ammonium compounds, as closely resembling those of sodium. Ammonium, (NH_4), this peculiar combination of nitrogen and hydrogen, acts, in its compounds, in all respects like a metal of the sodium group. Its hydroxide, although much behind sodium hydroxide, is an active base. Its salts are soluble and altogether comparable with those of sodium. Ammonium compounds of importance are; the hydroxide, ammonia water, useful for cleansing; ammonium carbonate, mentioned before in connection with baking powders; ammonium chloride, used in batteries and as a flux; ammonium sulphate, the convenient form for applying ammonia as a fertilizer. All these compounds dissociate readily into ammonia and the constituent acid.

CHAPTER XVI

THE METALS OF THE CALCIUM GROUP

THESE metals parallel the sodium group metals very closely, as is shown by the following comparison.

	Atomic Weight		Atomic Weight
Cæsium	133	Barium	137.4
Rubidium	85.5	Strontium	87.6
Potassium	39.1	Calcium	40
Sodium	23	Magnesium	24.3
Lithium	7	Glucinum	9.1

Magnesium and calcium are preeminent in this group as are sodium and potassium in the other. These four metals along with iron and aluminium are the common metals of the earth's surface, and they form the material environment of living organisms. The first four are found in the sea, the repository of much of the material leached out of the solid rock, but iron and aluminium, perhaps because they are so likely to form insoluble compounds, are not found there. If life originated in sea water, it is but natural that the four metals found in that medium should be congenial to living organisms, and normal to their existence, and, by the same token, all other metals would be abnormal and not compatible with their best development.

Calcium and magnesium are found in nature in strikingly parallel forms, both as silicates and in the secondary formations from them. They occur

as individual carbonates, and as dolomite, a combined carbonate, the latter in great abundance. They are both found as sulphates, calcium sulphate insoluble, magnesium sulphate soluble, the former known as gypsum and alabaster, the later as Epsom Salts.

In the metallic form calcium is interesting, but not practically important. Its properties are what one might expect from a member of the group following the sodium group. It is heavier and harder than sodium, oxidizes readily, burns, and takes the oxygen from water, but in all these reactions its activity is less than that of sodium. Magnesium digresses still further from sodium. It is reasonably permanent in the air, decomposes water slowly, even when the water is heated. But when ignited in steam it combines with the oxygen with some degree of violence. As magnesium is very light, only two-thirds as heavy as aluminium, it has come to be applied to the making of automobile parts. To a chemist who has known magnesium only as an active substance in the laboratory, it might seem that its activity is too great for ordinary uses. But the same is to a certain extent true of aluminium, yet it has been used for many years without any reports of disaster.

COMPOUNDS OF CALCIUM

Calcium oxide is the compound known as quick lime. Its great importance is due to the fact that it is so easily obtained from calcium carbonate, limestone, and when obtained is a substance of distinct chemical reactivity. Before the electrolytic methods were developed, this substance was at the basis of the alkali and soap industry, much as sulphuric acid

is at the basis of the acid industry. Calcium oxide, or lime, is made by heating the carbonate in lime kilns. Lime is used very little as the oxide, but is usually converted into the hydroxide by the addition of water, with which it unites with the evolution of considerable heat. This reaction is typical of the more active metallic oxides. The base formed, the hydroxide, possesses the active properties which are usually associated with lime. Lime is now being placed upon the market in the form of calcium hydroxide, because of the greater convenience and serviceability of that form.

Aside from the relation to basic substances, lime has two uses worthy of attention. One is the use in mortar. Its mixture with sand and water sets and then gradually hardens. The causes are not absolutely clear, but are probably associated with the slight, yet definite solubility of the hydroxide, and of the carbonate formed upon absorption of carbon dioxide from the air. A substance of limited solubility may dissolve and settle out again, with the result that it binds together any particles with which it comes in contact. Mortar is used less than formerly, as it is being replaced by Portland cement.

Another use of lime is agricultural. As organic matter in the soil decays, there is danger of an accumulation of slightly acid material. Lime neutralizes this as fast as it is formed, and its use for this purpose is steadily increasing. Finely ground calcium carbonate is also used, but its action is much slower than that of the more active and soluble calcium hydroxide.

The word lime is often used carelessly for any compound of calcium which may be present in water or in soil. The interest in all these cases is

in the calcium, and hence the misuse of the word causes little confusion.

Calcium carbonate, for a number of reasons, is one of the most interesting substances in nature. One reason has already been mentioned, that it is a common substance which is easily converted into an active reagent, lime. Another reason is its usefulness in a general way as the source of calcium compounds and of carbon dioxide, both very valuable. It is an abundant mineral, and, on account of its varying solubility under different conditions, results in many mineralogical and geological phenomena. Finally it is associated with many forms of animal life, seashell, coral, in a very interesting manner.

Calcium carbonate is only slightly soluble in water, 13 parts in one million. But when an excess of carbon dioxide is dissolved in the water, there is formed a much more soluble acid salt. Consequently such waters dissolve limestone rock and in course of time form subterranean passages and caves which are of great extent and interest. Again this soluble combination is easily broken up, so that the normal carbonate is redeposited, with the formation of stalagmites and stalactites, and cementing of fragments of limestone and other rocks into solid masses. The presence of the acid carbonate is the cause of the hardness of many natural waters, with the consequent inconveniences connected not alone with the destruction of soap, but also with the deposition of boiler scale, when the water is used for generating steam. For when waters containing this acid salt are heated, the acid salt is decomposed and the calcium carbonate is deposited as a crust. When waters contain a considerable amount of this, it

must first be removed to render it usable in boilers. The destruction of soap by hard waters, already discussed, is also a serious waste and nuisance, yet the softening of public water supplies is practiced to only a limited extent.

Certain animal organisms store up calcium carbonate in their shells. When the animal dies, this carbonate is for the most part permanently stored away in deposits of one kind or another, and in the end often forms solid rock. The coquina rock of Florida illustrates nicely the transition from shells to permanent limestone rock. In the same fragment shells may be seen and again the calcium carbonate so altered that it has lost all resemblance to its constituent shells. In these and other limestone deposits, the carbon dioxide of the atmosphere is being gradually stored away, and permanently withdrawn from the use of plants and animals. The supply is constantly being renewed by the combustion of coal and from subterranean sources. Unless the renewal equals the loss, it is conceivable that in the remote future living organisms will fail to find enough carbon dioxide to serve as the raw material for building up their tissue.

It is not desirable to describe other calcium compounds in too great detail. They are second only to sodium compounds in practical importance and a very brief statement concerning those of chief value will be sufficient. Almost all of them represent industries not alone of scientific chemical interest, but of very great practical importance, involving many large manufacturing establishments.

Calcium chloride, $CaCl_2$, has a striking affinity for water, tending to absorb it to pass over to the crystalline form, $CaCl_2.6H_2O$. It is hence much used

to dry gases and organic liquids, from which it readily absorbs the water. Calcium sulphate occurs in nature as gypsum $CaSO_4.2H_2O$, which loses part of its water on careful heating, thus forming plaster of Paris. Calcium phosphate is the important mineral constituent of bones, and in the form of a mineral is the source of the phosphate used in fertilizers. The natural rock is heated with sulphuric acid to render it somewhat soluble, and thus available for plants. Bleaching powder, $CaOCl_2$, involves calcium only as a means of holding the chlorine in a convenient form. Calcium carbide, CaC_2, is made as a source for acetylene, C_2H_2, as also for the purpose of fixing nitrogen in the cyanamide ($CaCN_2$) process. Calcium sulphite, $CaSO_3$, or its acid salt, is used in the disintegration of wood for the making of paper pulp. Finally, glass is a silicate of calcium and sodium, so important that it will receive special discussion in another place.

Not much more need be said of *magnesium* and its compounds. Magnesium oxide is used medicinally for the neutralization of acids. Such a use is not a purely isolated incident. It is based upon the position of magnesium in the whole series of metals. A base (for metallic oxides are practically bases,) derived from a metal preceding magnesium would be too active for medicinal use. One from a metal following would not be harmless. Magnesium in several respects has special uses, because it is last of the more active metals, not too active, yet active enough to accomplish what zinc and other metals following cannot do.

CHAPTER XVII

THE MORE ACTIVE HEAVY METALS

Aluminium	Chromium	Nickel
Manganese	Iron	Tin
Zinc	Cobalt	Lead

THE metals of this group (and we should here include copper from the next group) are the typical metals of the industries. They are reasonably abundant, they are so low in chemical activity that they endure the vicissitudes of ordinary use, and they possess the physical properties which are desired. Manganese, chromium, and cobalt do not count in respect to use as metals, except that the first two are alloyed with iron in certain forms of steel. Their chief value otherwise lies in their compounds.

All these metals are too active to be found free in nature in amounts which are more than curiosities. They occur mostly in combination with oxygen or sulphur, and are extracted from their ores in the regular way.

ALUMINIUM

Aluminium has some resemblance to the more active metals, and requires special treatment for its extraction. It is obtained by the electrolysis of the oxide dissolved in the fused fluoride. Obtaining the oxide in sufficiently pure form is the chief difficulty of the process. The advantage of alu-

minium for ordinary uses over other metals lies in part in its light weight, in part in its handsome appearance. Its specific gravity is 2.7, which is as high as that of stone. However, aluminium does not come into comparison with stone, but mainly with iron and copper, which are about three times as heavy. The light color of aluminium is not marred by the formation of the oxide on its surface, for the latter is colorless and transparent, thus altering the appearance very little. When aluminium was first introduced into the household, there were fears expressed that its high chemical activity would result in its dissolving in the acid juices of the foods. With ordinary care aluminium cooking utensils have proved to be altogether serviceable.

The high affinity of metallic aluminium for oxygen is made use of in the Goldschmidt method of welding. The finely divided metal is mixed with iron oxide. When this mixture is fired, the aluminium combines with the oxygen of the iron oxide with such great development of heat that the resulting iron is melted, and can be caused to weld together the parts of metal with which it comes in contact.

ZINC

Some of the chief uses of zinc are based upon its position in the electromotive series. It is one of the more active of the ordinary metals, and hence is used as an active metal in chemical laboratories, especially for the purpose of liberating hydrogen from acids. Its use in batteries depends upon this fact, as also its application in galvanizing iron. The use of the more active metal zinc in protecting iron, a less active metal, may seem paradoxical, but it acts as follows. Iron rusts on

account of its affinity for oxygen in presence of water. When iron rusts to a small extent, the rust spots formed act as nuclei for the rapid increase of the corrosion, and the rusting now proceeds much more rapidly. When the iron is coated with zinc, all initial oxidation affects the zinc and rust nuclei are never established. Zinc is frequently used much as an ordinary metal as it has desirable physical properties and is not very rapidly affected by water. Much is used in alloying copper to form brass.

IRON

Iron is first among the metals on account of its abundance and general usefulness. There are so many phases in the composition and uses of commercial iron that in the great field of industrial chemistry it forms a division of its own.

Iron occurs in large quantities as a minor constituent scattered throughout most rocks. In addition to these scattered masses, iron compounds form a number of abundant minerals. First comes hematite, iron oxide, Fe_2O_3, so called from its blood-red color. Even specimens which do not seem red show this color when finely pulverized, as when rubbed on a rough porcelain surface. Magnetite, Fe_3O_4, is attracted by a magnet and is a valuable ore. Masses of this which have become magnetic due to their location in the earth are called lodestones. Siderite, $FeCO_3$, and limonite, bog iron ore, $Fe_4O_3(OH)_6$ are less abundant. Iron pyrites, FeS_2, is a handsome mineral of metallic appearance resembling gold. It is valuable as a source of sulphur compounds, but the difficulty of removing all traces of sulphur prevents its use as a source of iron.

The chief chemical feature of the extraction of iron from its oxide is simple enough. The oxide is heated with carbon and the oxygen thus removed.

A. Pure iron is not sufficiently fusible to handle in a modern blast furnace. The iron is therefore combined with a certain amount of carbon and silicon, and the resulting metal, cast iron, is comparatively easily melted. It is cast, when made, into the so-called "pigs," or else is made directly into steel.

B. Carbon is introduced into the blast furnaces to serve a number of purposes. It supplies the fuel needed to give the required temperature; it unites with the oxygen of the ore; and it supplies the carbon for the compound mentioned in A. At the end of a number of chemical changes, much of the carbon finally emerges in the form of carbon monoxide, CO, still possessing considerable fuel value. This is utilized by being burned in great stoves filled with a checker work of fire brick, until these bricks are very hot. The air which is then fed into the furnace is preheated by passing over this checker work, and the heat of the carbon monoxide is thus utilized. This carbon monoxide is also utilized for fuel either by being burned under the boilers or in gas engines.

C. Mixed with the ore there is considerable earthy material not sufficiently fusible to melt and run out of the furnace. Therefore limestone is added to the ore and coke, in order to supply calcium oxide to make a readily fusible slag. This slag is occasionally run off from the top of the molten iron, and forms a considerable amount of by-product. This slag is used in various ways as a rock material for filling or ballasting and is in some places worked

over into useful products, glass or cement, by chemical manipulation. An important function of this slag is the protection of the molten iron from the action of the oxygen of the air blast.

D. The air blast gives the name to the blast furnace. In order to attain the necessary temperature, a blast of air must be blown in upon the fuel. Such a volume of air naturally has a serious cooling effect. By preheating the air by means of the stoves mentioned above, the cooling effect of the air is considerably diminished and the necessary high temperature more easily attained.

As was previously stated, the product of the blast furnace is not pure iron, but a compound with carbon and silicon. This has many uses, but for some purposes must be modified by the removal of these foreign substances. The different properties of the various compounds and mixtures, and the formation of these, make up the great study of iron and steel.

We will consider only a few phases of this complex chapter. When we have the compound called cast iron, we have the following conditions and properties. Cast or pig iron contains as much as 5 per cent of carbon. It is fusible in foundry furnaces and can be thus used for making castings, a rapid way of shaping iron; it is hard, but brittle; it is not forgeable or weldable; only in masses will it endure a strain.

On the other hand, when practically all the carbon and silicon are removed, the following properties are found in the resulting wrought iron. It is no longer easily fusible; it is comparatively soft, but very tough, of high tensile strength, and no longer brittle; it can be forged and welded.

These properties of pig iron and wrought iron are seen to be supplementary to a striking degree, and the two forms of iron are used in accordance with these properties.

Wrought iron is made rather little now, as steel, to be described presently, serves most of its purposes. It was made by adding oxygen to molten pig iron until the carbon which gave the characteristic properties was burned out. The wrought iron was then taken out and rolled, forged, and shaped, casting being no longer possible.

Steel is an intermediate substance between these two forms, possessing intermediate composition and a combination of the properties of each in such a great degree that it has become of the utmost importance. Steel was made years ago by adding the right amount of carbon to wrought iron, but the method was slow and the product irregular. Yet wonderful results were attained.

It was the invention of the Bessemer process which revolutionized the steel industry. Bessemer argued that a quick way to make steel would be to blow air through molten pig iron until just the right amount of carbon was burnt out. His supposition has proved to be a correct solution of the problem, and steel can thus be made with great rapidity. The molten iron is placed in egg shaped "converters" and air blown through for the proper length of time. The product is modified at the end by the addition of manganese, carbon, and silicon, so that the proper proportions are attained. The following is a summary of the properties of steel. It must be remembered that steel includes all gradations from the carbon-free wrought iron on the one hand to a high carbon steel on the other.

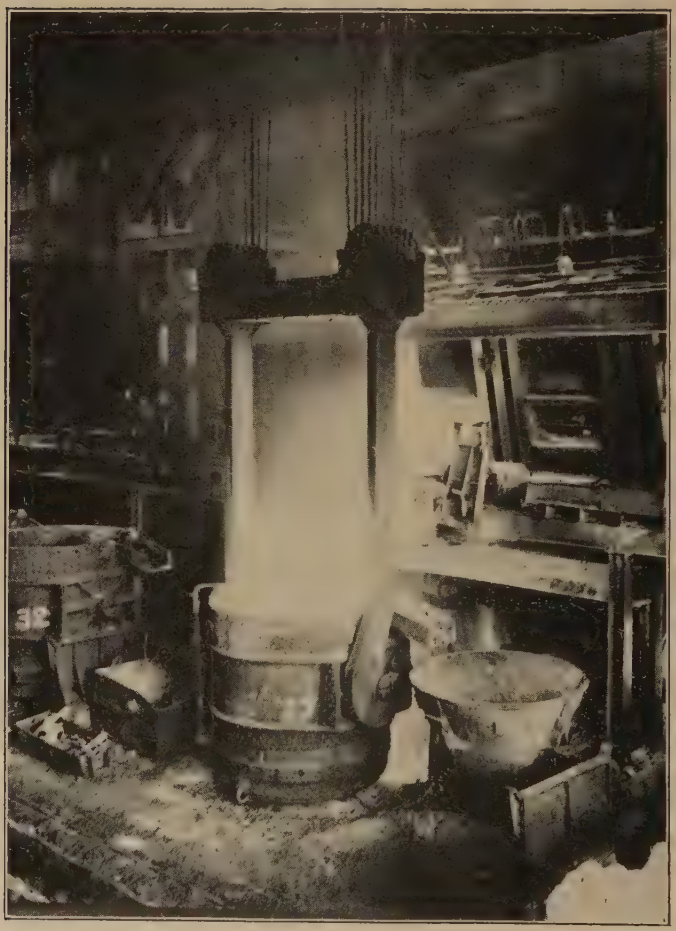
Steel is more fusible than wrought iron. Fusion, or melting, is a convenient way of handling the metal. Steel is harder than wrought iron, it can be forged, and is very strong. According to its carbon content, it is harder and more brittle, or softer and more malleable, all gradations being prepared for the great variety of uses. Other elements also are influential in the properties of steels.

The open-hearth process of steel making depends upon the successful development of very high temperatures and control of the operation throughout. The choice of raw material for this method is capable of wide variation. If iron low in carbon is used, pig iron, supplying more carbon, may be added. If the carbon is too high, iron ores may be added to supply oxygen to burn out this carbon. Before the metal is cast, it is possible to make check tests, assuring the proper carbon content of the product.

In a superficial discussion of steel, its composition may be said to be an iron containing a certain proportion of carbon. But steel as now made and used is a very complicated and variable substance. In making various steels, silicon, manganese, nickel, vanadium, chromium, tungsten, molybdenum, titanium , and uranium are used. By help of the microscope different constituents of steel have been identified, such as ferrite, which is pure iron, graphite, pure carbon, cementite, a carbide of iron, Fe_3C, perlite, a mixture of ferrite and cementite of constant composition. Other substances not so clearly defined are present. The properties of steel are determined by the nature and proportions of these constituents and their relations to each other.

The compounds of iron present one point of interest, not peculiar to iron, but most conspicuous

INTERIOR OF STEEL MILL, SHOWING THREE BESSEMER CONVERTERS, ONE TILTED



POURING STEEL INTO A LADLE—OPEN-HEARTH FURNACE

with this metal. Iron forms two classes of compounds, in that it combines with oxygen and other negative groups in two proportions. Such compounds are:

Ferrous oxide, FeO	Ferric oxide, Fe_2O_3
Ferrous hydroxide, $Fe(OH)_2$	Ferric hydroxide, $Fe(OH)_3$
Ferrous chloride, $FeCl_2$	Ferric chloride, $FeCl_3$
Ferrous sulphate, $FeSO_4$	Ferric sulphate, $Fe_2(SO_4)_3$

In ferrous compounds the iron functions with a valence of two, in the ferric, of three. Ferrous compounds are usually white or pale green in color while ferric are yellow, brown, or red. It is therefore easy to recognize them. Ferrous compounds remain ferrous in the usual transformations of chemistry, and the ferric remain ferric, unless a definite change, called oxidation or reduction, transfers them from one class to the other. In nature this is seen often when the ferrous compound of a grayish clay or rock, upon exposure to the air, gradually oxidizes. There is then formed the ferric compound with the characteristic red or yellow color.

TIN

Tin is found mainly as tinstone, SnO_2, and is extracted in the usual way. It is a handsome metal and as it is fairly well down in the electromotive list, it is not readily attacked by oxygen or other reagents. It is therefore rather permanent and is used as a protective coating for iron. Sheet tin is iron thus coated, and the making of this constitutes its great use. Pure tin, called block tin, to distinguish it from the tin coated sheets of iron, is often used in special apparatus, where an inactive metal is needed. Tin has a low melting point, and therefore, mixed with lead, is valuable for solder.

LEAD

Lead is more abundant than tin and is used in a greater variety of ways. It is less active in some respects, but with some substances, water and carbon dioxide for example, it does corrode. As lead is used much for water service, and it is so poisonous, this question of corrosion is an important one. A redeeming feature in the use of lead is that the ordinary impurities of water often cause the formation of an insoluble coating on the inside of the pipe, so that the water has no further action. Lead is a silvery white metal, and the general impression of its dull color is due to the coating of oxide formed on its surface. The uses of lead depend in part on its physical properties. It is heavy, and therefore used for weights, shot and such purposes. It is soft and easily handled, so used for pipes. It has a low melting point, for which reason it is used in solder. Other uses are based in part on its chemical properties. Its low chemical activity and insolubility of its compounds make it useful for such purposes as tanks, chambers, and pipes in acid factories, as the acids corrode it only slowly.

Useful compounds of lead are many. White lead is the commonest of the solids mixed with linseed oil for the making of paint. It is a basic carbonate, that is, partly lead hydroxide, and partly lead carbonate. The virtues of white lead are its clear white appearance combined with opaqueness, so that a thin layer spread over a surface conceals what lies beneath. Red lead, Pb_3O_4, has a fine red color and is used in paints for that reason. Lead is a constituent of other pigments, as chrome yellow, $PbCrO_4$.

CHAPTER XVIII

THE LESS ACTIVE METALS

THIS list includes copper, arsenic, antimony, mercury, silver, platinum, and gold. Within the group there is considerable variation of activity. The chemical activity and compounds of copper are of distinct importance, while gold and platinum are so inactive that their compounds are few and unimportant. From the standpoint of the chemist, copper is the most interesting of the group.

COPPER

Copper has much in common with the last metals of the previous group. Yet in the matter of occurrence in nature there is a marked deviation, for copper occurs as the free metal in great abundance. The Lake Superior mines, yielding free copper, are famous, although the greater proportion of all the copper mined comes from the sulphide. The advantages of copper over other metals are in part apparent, and in part require technical knowledge to appreciate. It is handsome, and even if not permanent in the air, it may be cleaned easily, and its beauty restored. When used for such purposes as roofing, it corrodes only superficially, with the formation of the beautiful green basic carbonic, an appearance which is welcomed. Copper alone and in

the form of brass lends itself to the making of delicate parts, as, for example, electrical apparatus. Cooking utensils on a small and large scale, for home and factory use, are often made of copper and are very permanent. Its high conductivity for electricity makes it the most used of the metals for this purpose. Its alloys are numerous and much used, among them are brass, bronze, German silver, gun metal, and the alloys of gold, silver, and nickel used in coinage. Alloys consume more than half the amount of copper produced.

In addition to the important interests of copper just enumerated, its properties suggest relations between chemistry and electricity which are so important that we must give them somewhat thorough consideration. The chief point at issue is that copper is the lowest of the more available metals in the electromotive list; it is the least active, that is, it tends least of all of them to go into combination. This, as will be seen, is closely related to the development and application of electricity.

The relation between heat and chemical changes runs through all our discussion of chemical phenomena. We also make frequent mention of the relation of electricity and chemical change, and the metal copper is used so much in this connection that this is a convenient place to study the subject.

ELECTROPLATING

It will be desirable to recall the simpler details of electrolysis. If we dissolve copper chloride in water, the salt is ionized into its positive and negative ions, Cu^{++} and $2Cl^{-}$. If now we introduce the elec-

trodes from a battery into this solution, the positive copper will be attracted to the negative electrode, and the negative ion to the positive electrode. As the ions arrive at the respective electrodes the charges upon them will be neutralized and the copper and chlorine left in the form of elements. The copper will deposit and the chlorine escape. With slight

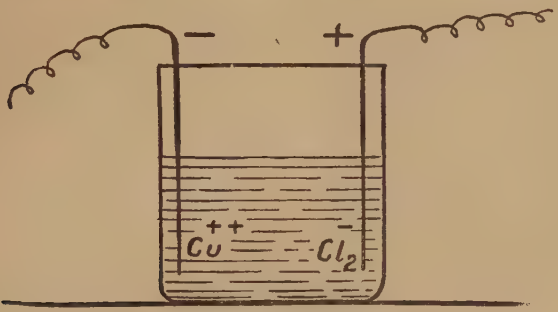


DIAGRAM ILLUSTRATING ELECTROLYSIS OF SALTS, ELECTROPLATING AND ELECTRO-REFINING

In every case the ions are attracted to the poles of opposite charge.

modification this operation can be converted into one of copper plating.

For the latter operation the object to be plated with copper is suspended in the solution as the negative electrode, and a plate of copper of considerable amount made the positive electrode. As the current passes the copper is deposited in the usual manner on the negative pole, that is, on the object to be plated. The negative chlorine ion travels to the positive pole, but instead of being discharged combines with the positively charged copper, to form copper chloride which replenishes the solution. From the solution the copper continues to be deposited on the negative pole, and from the positive pole—the

plate of copper—the copper continuously passes into solution. The final result is that the copper passes from the plate of copper forming the positive electrode, to the object to be plated, forming the negative electrode. Except in details the plating of other metals is the same as this.

ELECTRO-REFINING

Another application of these ideas is that of electro-refining applied especially to copper. Again we take a solution of copper chloride. A thin sheet of copper, simply to serve as a foundation, is made the negative pole, while the heavy bar of copper which is to be refined is made the positive pole. As the current passes the salt in solution is electrolyzed and copper is deposited upon the negative pole, while the chlorine ion collected at the positive pole attacks the copper there and causes it to go into solution. Now comes the differentiation between copper and the other metals, which are the impurities to be eradicated. As the chlorine attacks the positive pole, only copper and the more active metals above copper in the electromotive list go into solution. In presence of a metal high in the list, the less active metals remain in the metallic form, and inasmuch as the bar of copper is disintegrating, due to its solution, they are released and deposit at the bottom of the tank in the form of a sludge. Thus the copper is separated from all metals of lesser activity. At the negative pole, on the other hand, only the copper is deposited, for here only the less active metals can leave the solution. But the less active metals of the positive pole never went into the solution, consequently the copper alone can

deposit and the more active metals are left in the solution in the form of chlorides.

BATTERIES

Another application of this relative activity of the metal is the primary cell. We are now turning the matter about and converting chemical energy into electrical energy. The Daniell cell will illustrate our point. This consists of a dilute solution of sulphuric acid, in which are suspended a plate of zinc, high in the electromotive list and a plate of copper, low in the list. They are connected outside the solution with a wire to establish electrical connection. On account of its high solution tension (activity) the zinc tends to go into solution, that is, to form zinc sulphate. But in zinc sulphate, ionized as it is, the zinc ions must take on a positive charge, and to accomplish this the zinc plate must take on a negative charge, much as a boat is driven south when a diver leaps from it to the north. The hydrogen of the acid is now left unprovided for and is liberated at the copper plate. While in solution the hydrogen ions are positively charged, and to come out of solution the hydrogen must lose its charge, which is given up to the copper plate, which thus acquires the positive charge. Thus the zinc plate is continuously charged negatively, and the copper plate positively. This means the establishment of a current.

Another case is the secondary or storage battery. This consists, with many mechanical refinements, of two plates which, when the battery is charged, consist, the one of lead, and the other of lead peroxide, that is, one plate contains no negative group in combination with the lead, the other a

double portion. Work comes from inequality of conditions. The steam engine has high pressure within the boilers, low pressure without. Water power represents the same thing and the work is done by the equalization of these unequal conditions. When the battery is discharged both plates become equalized, in that they both consist of lead sulphate. The mechanism of the discharge is as follows:

The two plates, one lead, Pb, the other lead peroxide, PbO_2, are immersed in dilute sulphuric acid. The surplus oxygen of the peroxide takes up hydrogen from one molecule of the sulphuric acid forming water. But in this combination the hydrogen is, so to speak, un-ionized; that is, loses its charge, which is passed over to the plate, which thus becomes positively charged. This leaves the sulphate of the acid unprovided for and it combines with the lead of the other plate. In doing so it is un-ionized in its turn, so that this plate receives a negative charge. The first plate then is continuously receiving positive charges from the hydrogen, the other is continuously receiving negative charges from the sulphate, and this means the passage of a current. The residual lead oxide is promptly converted into lead sulphate according to the simple chemical reaction, $PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O$. Both plates are now in the form of lead sulphate and the battery is discharged.

To recharge the battery the first of the plates mentioned above is connected with the positive pole of a source of electricity, and the other plate is connected with the negative pole. When a current is passed the positive pole attracts negative ions in the regular way from the sulphuric acid present, and the positive, $PbSO_4$, plate becomes $Pb(SO_4)_2$.

This compound cannot persist and decomposes into $PbO_2 + 2SO_3$; the former represents the form of the plate in the charged battery, the latter unites with water to form sulphuric acid, $SO_3 + H_2O \rightarrow H_2SO_4$. At the negative pole the hydrogen ions of the sulphuric acid are attracted, and upon reaching it remove the negative SO_4 ions from the plate, forming sulphuric acid and leaving the plate in the form of lead. The battery now stands, PbO_2, lead peroxide on the one hand and, Pb, lead on the other, the state of inequality necessary for work. The solution of sulphuric acid is now more concentrated, as all the SO_4 ions are in the solution. It is well known that the readiest way to tell whether a battery is charged or not is by the amount of acid present in the solution.

ARSENIC AND ANTIMONY

These metals are interesting in that they are brittle and show some of the properties of the non-metals. The greatest interest of arsenic outside of its purely scientific interest lies in the poisonous nature of its compounds. It is therefore used as an insecticide for spraying foliage to kill leaf-eating insects. Paris green and lead arsenate are the forms applied. Their frequent application in this respect gives rise to some solicitude as to whether the arsenic thus scattered around will presently be a menace to men and cattle. It seems likely that this will not be the case, as it will probably be dissipated beyond the point of danger. The menace, however, must never be forgotten. Antimony is used in alloys to give hardness. Its compounds are used to some extent in the match industry and for giving certain qualities to rubber.

MERCURY

Mercury is remarkable for its liquid state, and also for the fact that its compounds are easily decomposed. The decomposition of mercuric oxide by heating and the consequent discovery of oxygen is a classic in the study of science. The liquid state of mercury is the reason of its great usefulness in physical apparatus. The use in thermometers, in barometers, and in apparatus for the handling of gases is of the highest importance. This fact is also at the basis of its use in the recovery of gold and silver. As solvent for these metals it simplifies their extraction, and 40 per cent of the mercury mined is used in this way.

Mercury compounds are very poisonous. They are therefore used as antiseptics and disinfectants, the most valuable being mercuric chloride, "corrosive sublimate." Mercury has some application in medicine as, for example, calomel, mercurous chloride. Mercuric sulphide as ordinarily prepared in the laboratory is of an uninteresting black color, but when prepared in a special manner it forms the brilliant vermilion of commerce, and the preparation of this pigment constitutes one of the great uses of mercury. When thus used, as is the case in the use of copper as a fungicide, the metal is permanently lost.

SILVER

Silver has three main fields of interest—ornamental ware, coinage, and photography. The last of these is of the greatest chemical importance, but the chemist cannot neglect the other two altogether. Silver is found as silver sulphide, and if the ore were pure it would be an exceedingly simple matter

to extract it. But silver ores are very lean. An ore producing twenty ounces of silver to the ton might be valuable enough to work, yet it would have a silver content of less than one-tenth of one per cent. To recover this a large amount of useless material must be handled. The methods of extraction lie without the scope of this work.

For coinage and plate, silver is usually alloyed with 10 per cent of copper, and this is the sterling silver of commerce. The beauty of silver lies in its whiteness. It is the whitest of the metals and does not corrode except in the presence of sulphur or sulphur compounds. It is then easily cleaned. The high reflecting power leads to the making of mirrors by the coating of glass with silver. A solution of silver nitrate in ammonia is virtually silver oxide, Ag_2O. When heated with substances like grape sugar, or formaldehyde, the latter extracts this oxygen in such a way that the silver is deposited in the smooth, even layer which constitutes the mirror.

THE CHEMISTRY OF PHOTOGRAPHY

Silver compounds are not the only substances which respond to the chemical stimulus of light. Compounds of iron, mercury, and other metals are acted on, and the whole process of plant growth is dependent upon light. But silver compounds are the most sensitive and the most used. Silver further is readily thrown out of its compounds in the form of an opaque powder, so that it is easily made into an image. The light which is most effective is the portion of the spectrum at the violet end and beyond. Light weak in these rays is ineffective, as is illustrated by the red light of the dark room. Flaming

arc, mercury, and magnesium light are rich in these rays and may be used for photography in the absence of sunlight.

The camera and its use come under the head of physics. The lens serves to throw upon the plate the exact image of that which is to be photographed. Our chemical story begins then with the projection upon a plate of an image, that is, light of varying degrees of intensity. The plate is made up of a film of gelatine, filled with silver bromide. The silver bromide is acted on in proportion to the intensity of the light which falls upon it, although an inspection of the plate reveals no change. It is likely that there is formed a limited amount of silver subbromide. This operation is the exposure and the image is called the latent image. It is an image only in its possibilities. If this exposed plate is now immersed in a solution which has a reducing action, it will take from the silver the bromine with which it is combined, in proportion to the amount of the action of the light, and there will be deposited a corresponding amount of silver, in finely divided form, very black and opaque. We now have a real image, but dark where the object was light, and light where the object was dark, so that it is called a negative. Much of the original silver bromide is still unchanged, and this must be removed, or in course of time it would change under the influence of light and blacken the whole. The removal of this residual bromide is called fixing and is accomplished by immersing the plate for a while in a solution of sodium thiosulphate ("hypo"), which changes the silver bromide into a soluble compound, to be later washed out. When dried, the plate is ready for printing.

Printing on the whole is accomplished according to one of two methods, the printing out and the developing. In the former the paper is covered with silver chloride which blackens under the influence of light, due to the formation of mixed oxygen compounds. The paper is put in the sunlight under a negative and printed until done. Such prints are toned, that is, immersed in gold and other solutions, so that new compounds are formed with more pleasing colors. These prints must be fixed as are the plates by the removal of any silver compounds not acted on. The developing papers are similar to the plates, only not nearly so sensitive. There is first formed the latent image, which must be developed and fixed like a plate. The great advantage of this process is that artificial light is quite adequate to make the impressions, whereas the printing out papers need sunlight. There are, of course, endless refinements and details. The above are the main features.

PLATINUM

Platinum is the most important of the platinum metals. There are six of these, falling into two groups, those with atomic weights about 106, ruthenium, rhodium, and palladium, and specific gravity about twelve, and the other set, osmium, iridium, and platinum, with atomic weight about 200, and specific gravity about twenty-two. They all have a high melting point and low chemical activity. The uses of platinum are of two types, the first being for crucibles, as the metal does not melt readily and is stable to most reagents. But many a crucible has been ruined because the operator assumed that platinum was inactive to everything. The other

property is the high value of platinum as a catalyzer. This applies especially to the contact process for the manufacture of sulphuric acid. As platinum is of unique value for chemical manipulations, its use for jewelry is frowned upon by chemists, who find satisfaction in calling attention to the fact that the beauty of platinum was not appreciated when it was comparatively cheap.

GOLD

Gold naturally attracts much attention. Its great beauty, rarity, and durability result in a high estimate of its value. It is the least active metal on the list and is attacked by only a few reagents, particularly chlorine and mixtures which yield chlorine, like aqua regia, a mixture of nitric and hydrochloric acids. The compounds of gold are of minor importance. The obtaining of gold from its ores is a fine illustration of the importance of engineering as compared with pure chemistry. Some gold ores yield only a tenth of an ounce of gold to a ton of ore. To make this extraction profitable is not a simple matter. Gold extraction is partly mechanical, especially with the help of the solvent action of mercury, and in part chemical, the gold being put into solution by the action of chlorine or of potassium cyanide. This last process has done much toward making lean ores available, as it enables large quantities of ore to be handled at low cost.

CHAPTER XIX

CLASSIFICATION

IF the study of chemistry were the mere acquaintance with a large number of isolated facts, knowledge of a number of disconnected elements, and acquaintance with reactions which varied with every set of substances which came together, the whole would be a hopelessly confused mass of information which would lead us nowhere. Our subject would not be a science and would be unworthy of the high esteem in which it is held. Chemistry is not disconnected. The veriest beginner will find general principles at once, and if he appreciates an action for one substance, will look for a similar action in the next, and will not be disappointed. Our subject is an orderly one, and even if there is some danger that too many facts will stand out by themselves, the general order of the subject should be looked for conscientiously.

The first conception of the elements is that they are the absolutely distinct chemical units from which compounds are derived. If we begin with different elements we obtain different compounds, and from the same compound we must always come back to the same element. We assume that the element, that is, the atom of the element, never changes. The atom is constant through all our manipulations, and no matter how much we build

up and tear down we must come back to the original. The eighty odd elements might indicate eighty different lines of experience, each element a law unto itself. But a very cursory glimpse at chemistry shows that the different elements, although always absolutely distinct and unchangeable, are not laws unto themselves, but that they are strikingly similar, and react in a similar manner to a remarkable degree. The similarity of the elements is shown most promptly by the metals, which form a group with striking physical and chemical resemblance. Among the nonmetals the members of the halogen group are very much alike. They are so regular in their properties that, given the characteristics of one, those of the others may be anticipated. Of more striking value than the qualitative resemblance is the numerical relation of their atomic weights. This regularity is repeated a number of times. We have sets of elements which show this numerical relation.

The Halogen Group	The Sodium Group	The Calcium Group
Fluorine 19	Sodium 23	Magnesium .. 24.3
Chlorine 35.5	Potassium 39.1	Calcium 40
Bromine 80	Rubidium 85.5	Strontium ... 87.6
Iodine 127	Cæsium 133	Barium 137.4

The increase of atomic weights is the same in all of these groups. The difference is sixteen between the first two and about forty-five between the others. These differences occur so frequently that they may be considered regular.

Facts like these are bound to lead to speculation as to their cause. What is this relationship between the different elements? It is altogether evident that the elements are not absolutely independent.

Early in the nineteenth century, Prout's hypothesis aroused much interest and in the way of suggestive speculation does so still. At that time the atomic weights of the elements, referred to hydrogen, seemed to be whole numbers. Prout's hypothesis was that the different elements were made up of hydrogen as the constructive unit. Later work on atomic weights has shown conclusively that their weights are not really based on hydrogen as a unit. The hypothesis cannot be correct, but the germ of the idea is a valuable one, and we will come back to it.

A rough classification of the elements into the metals and the nonmetals has been in constant use in these pages. So also a further classification into such groups as the halogen group, the sodium group, and the calcium group.

So far as they go these groups are most useful and much of our work is based upon them. But the periodic classification now to be described comprehends all the elements in one complete system. This was published in 1869 by Mendeléeff and Lothar Meyer independently. It is so valuable and satisfactory that it has been universally adopted and remains the corner stone of all broad conceptions of the elements and their relations. It may be stated thus: The elements are written down in the order of their atomic weights. These are values which have been determined with the greatest accuracy, and on the whole are reliable. It will then be noticed (leaving hydrogen and the rare gases out of consideration for the present) that after the first seven have been considered, the eighth, sodium, is very similar to lithium, the first one considered; the ninth is similar to the second, and so on, until

we come to the fifteenth, potassium, which again resembles the first, and this repetition of resemblances continues, when certain modifications and omissions are made, right on through the whole list of elements. Because the properties thus repeat themselves in regular periods, this classification is called the periodic classification.

Group	0	I	II	III	IV	V	VI	VII	VIII		
Typical Compounds	None	$NaCl$ Na_2O	$MgCl_2$ MgO	$AlCl_3$ Al_2O_3	CH_4 CO_2	PH_3 P_2O_5	H_2S SO_3	HCl Cl_2O_7			
Valence to H		1	2	3	4	3	2	1			
Valence to O		1	2	3	4	5	6	7			
1st Short Series	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19			
2d Short Series	Ne 20	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35.5			
Long Series	A 40	K 39.1	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7
		Cu 63.6	Zn 65.4	Ga 70	Ge 72.5	As 75	Se 79	Br 80			
Long Series	Kr 83	Rb 85.5	Sr 87.6	Yt 89	Zr 91	Cb 93	Mo. 96		Ru 101.7	Rh 102.9	Pd 106.7
		Ag 108	Cd 112	In 115	Sn 118.7	Sb 120	Te 127.5	I 126.9			
Long Series	Xe 130	Cs 133	Ba 137.4	Rare earths 139—175		Ta 181.5	W 184		Os 191	Ir 193	Pt 195
		Au 197	Hg 201	Tl 204	Pb 207	Bi 208					
	Nt 222		Ra 226		Th 232		U 238				

A number of discrepancies were apparent at the time, and others have developed since. Some of these have been cleared up, others are still outside our understanding. But by bravely facing them, not trying to explain them away, by accepting what was evidently right, leaving the doubtful to future enlightenment, we find the classification of pre-

eminent usefulness as a summary of what was known before, and an inspiration for research work.

From a consideration of the table as shown, the following striking facts stand out:

A. The elements, considered from the standpoint of their atomic weights, and arranged in that order, are comprehended in one complete scheme, showing a periodic recurrence of properties.

B. Of the series thus established the first and second each include seven elements comprising the short series. The third and fourth short series are needed to form together the long series. The regular variation and periodicity applies in some measure to these two short series, but the full rounding of the period does not come until the end of the long series. At the middle portion of the long series occur groups of three elements strikingly alike—an exception to the usual variation.

C. The atomic weights increase from element to element by small increments. Owing to the periodicity, the atomic weights of similar elements differ in a regular way. At first the increment is sixteen, but after the third short series, following only those elements which are on the right or left of each column, the increment is about forty-five. From fluorine to chlorine the increment is sixteen, the weights being respectively 19 and 35.5, whereas bromine and iodine show increments of about forty-five. The eighth column shows a different principle, in that similar elements vary little in their atomic weights.

D. The variation in valence is regular. Since valences are variable, and frequently are higher in respect to oxygen than to hydrogen, the higher is usually assumed to be the true expression of valence.

In the classification the valence of the elements in the different columns is found to increase from one to four when considered with respect to hydrogen, and then to drop back to one, whereas the valence toward oxygen increases steadily up to seven. The valence of the eighth group should perhaps be left outside of this brief consideration, but it is interesting to observe that the only elements, osmium and ruthenium, which do have a valence of eight, fall into this group.

E. The common and active metals have low atomic weights and fall into the first part of the table. Iron, fifty-six, has the highest weight of the abundant elements.

F. When this table was first proposed there were no elements in the places now occupied by scandium, gallium, and germanium. Mendeléeff predicted the discovery of elements which would fulfill the conditions required by these positions, and he outlined in detail the properties of such elements and their compounds. The elements thus predicted were discovered in the course of the next decade and confirmed Mendeléeff's predictions to a remarkable degree. The table can then anticipate and suggest future discoveries, both of unknown elements, as well as of the properties that any missing elements would possess. It is also a check on facts already supposed to be known. For example, the atomic weight of glucinum was corrected from 13.5 to 9, as a result of its fitting in a place in the second column suggested by the value 9, while for the value 13.5 there was no vacancy.

G. Inasmuch as metals as a class have lower valences than the nonmetals, the metals are more

likely to be found in the first columns, and the nonmetals in the later columns. Further, in any given group, or column, the more metallic element has a higher atomic weight and the more characteristic nonmetal the lower. Potassium is more characteristically metallic than sodium; so on the other hand chlorine is more characteristically nonmetallic than bromine. Therefore the metals, in case of doubt, are near the lower portion of the columns, as the nonmetals are near the upper portion. Combining these two principles a diagonal may be drawn across the table from a point above glucinum to a point below iodine. The metals on the whole will be found below this line, the nonmetals above, and the doubtful elements near it. (Omitting Column VIII.)

H. When argon, the first of the rare gases of the atmosphere, was discovered in 1894, no place was found for it in the table as then accepted. It was finally placed in a column preceding the first, the so-called zero column. Thus the way was opened for the investigations which presently resulted in the discoveries of the other rare gases. This column was in the end filled out as completely as were the others. The complete lack of chemical activity falls in with the suggestion that their valence is zero, as indicated by their position.

I. The periodic arrangement causes the elements to fall into groups, which are represented by the columns. After the second short series, the elements of the first half of the next long series are written to the left, those from the second half to the right. The true groups are made up of the metals directly under each other, so that there are in each column two related groups. In each group

the properties vary with great regularity as we advance in the atomic weight. We thus have a number of groups, in each of which the properties as a whole, and their variation within the group, are determined according to very definite principles.

J. The discrepancies of the classification. The use of the double series after the second, and the grouping of certain elements, not otherwise fitting in, in the eighth column, and the location of the inert gases in the zero column, are no longer looked upon as irregularities. These arrangements fit in admirably, now that they are better appreciated, and instead of detracting from the good order of the whole, they have aided much in their suggestiveness. But the inversion of the order of atomic weights for tellurium and iodine still stands as a striking exception. Nevertheless, no confusion comes from accepting this exception, and it is the part of wisdom to adopt the usefulness of the rest and leave the explanation of the doubtful features to the future. The same fact is to be observed in the case of argon and potassium. There were reasons for placing argon in a place after fluorine, assuming a weight of 20, instead of 40. This would have avoided this discrepancy. When, however, argon was finally placed before potassium in the zero column, this position was soon justified by the discovery of the other members of the group.

There is a group of metals, called the rare earths, with a valence of three and having atomic weights of from 140 to 180, which have not been satisfactorily placed.

There is no place for hydrogen in this scheme. Hydrogen is so unique that we may tentatively as-

sume that it occupies a place by itself, or we may look to its proper placing in the course of time.

Many modifications of the plan as here given have been proposed. The main principle of the periodic classification is retained in all of them.

ATOMIC NUMBERS

Since 1913 another light has been thrown upon this question of the periodic arrangement by the study of X-ray spectra of the elements. These are obtained by photographing a diffracted X-ray beam which had impinged upon the element, much as the usual spectrum is obtained and photographed. From the study of these spectra, it is seen that the elements fall into a regular order near to that of the periodic classification, and from this order they receive a number called the atomic number. The numbers run from 1 for hydrogen to 92 for uranium. From a consideration of these new ideas, the following facts stand out.

The general ideas of the periodic classification are confirmed. The anomalies noted in the three cases, argon and potassium, cobalt and nickel, tellurium and iodine, disappear, as the atomic number calls for the accepted arrangement based upon chemical properties. It would seem, then, that the atomic weight only approximately determines the position of an element: that the exact position is determined by other factors, suggested by these X-ray spectra. The total number of elements is determined by the atomic number of uranium as 92. This sets a limit to the possibilities, and the search for new elements will have some guidance, a fact which will be of especial value in the study of the confused chapter of the rare earth metals.

CHAPTER XX

SUGGESTIONS FROM THE STUDY OF THE RADIOACTIVE ELEMENTS

WITH the discovery of radium and the study of radioactivity, has come a new aspect of matter and a corrected idea of the structure of the atom. It has never been reasonable to suppose that the atom was a simple indivisible material affair.

Radium as a metal belongs to the calcium group, most nearly resembling barium, and it exhibits properties such as we would expect from its position in the periodic table. The high atomic weight is striking, and its radioactivity marks it as distinct from the usual type of element. The conspicuous signs of this radioactivity are that its compounds are self-luminous and give off heat, the rays emitted make an impression upon the photographic plate, and they cause gases to become conductors of electricity. They bring about certain other physical and chemical changes, such as the fluorescence of the X-ray screen and the decomposition of water. Thorium and uranium, also with extreme atomic weights, are also radioactive, although in a lesser degree. That a substance should spontaneously evolve energy without itself showing a change was startling indeed, and seemed to negative the law of the conservation of energy. A natural interpretation, but subsequently shown to be untenable, was that radium

acted as an agent for the collection and transforming of the inconspicuous energy of the surroundings, to give this off again in the more conspicuous forms which mark the properties of radium. But this explanation soon yielded to the disintegration theory.

The disintegration theory is that the highly complex atoms of the radioactive elements are breaking down into simpler atoms. In this process they give off radiations which consist of the alpha rays (atoms of helium), of beta rays (negatively charged electrons), and of gamma rays, akin to the X-rays. As the result of the loss of the helium or the electron, there results another atom, in the former case with an atomic weight of 4 less, in the latter case with practically the same atomic weight. This atom in turn disintegrates in a similar manner, and this goes on until there is reached a product of sufficient simplicity and stability to resist any further disintegration tendency. The various products are mixed, possess varying rates of speed of disintegration, and the interpretation of the whole is far from simple. A crude scheme of the changes is the following: Uranium, with an atomic weight of 238, upon disintegrating, forms a modified uranium atom, weight 234. This leads to ionium, 230, this to radium, 226, to niton 222. Then follow other atoms, called radium A, B, and C, each 4 units lighter than the one before until the changes cease and the product cannot be determined. It is reasonable to suppose that this final product is one of the ordinary elements, lead, for example.

This list leaves out of consideration the products which are of atomic weight similar to the parent substance, in that the loss is simply that of an

electron (negative electricity), and not an atom of helium. But it is impossible without going into long discussions to follow this out further. The final conclusion is well established, namely that the most complex atoms have an inherent instability, so that they spontaneously disintegrate, losing helium and electrons. This disintegration continues until a point of stability is reached. Thorium and uranium seem to be original parent substances; the others, including radium, exist only in passing. They come from some predecessor, and disintegrating, form another element of lower atomic weight.

No force so far applied in the laboratory has been influential in accelerating or retarding this action. It is absolutely without our control. Nevertheless, it is legitimate to attempt to disintegrate atoms beyond the range of this spontaneous disintegration, as well as to try to build up the more complex from the simple elements.

The amount of energy liberated when these changes occur is tremendous and has aroused much comment, especially of the popular order. It is said that 1 gram of radium will give out 100 gram calories of heat every hour during its life, which is about 2,000 years. But we are not unfamiliar with the fact that when we change from one form of expressing a given amount of energy to another, we observe the same effect. One gram of charcoal, upon being burned, that is, on conversion of its chemical energy into heat energy, yields about 8,000 calories, that is, heat enough to elevate the temperature of 8,000 times its mass of water 1 degree C. Further, when this heat energy is converted into mechanical energy, there is another striking "stepping up," for this amount of heat is capable of lifting 340 million

grams of matter 1 centimeter. The chemical energy of one gram of carbon expressed in terms of work gives us a very large number. In comparison with these numerical relations, the numbers obtained by converting disintegration energy into the familiar heat units are not incomprehensible. The stepping up from disintegration energy to chemical energy, (taking the chemical energy in one gram carbon as an example,) is about 200,000, from chemical energy of carbon to heat energy, about 8,000, from heat energy to mechanical energy about 40,000, our numbers being restricted to grams and centimeters.

The great regularity of relationships brought out by the periodic table among the elements has time and again suggested the complexity of the atom and the building up of the atoms of similar elements from a primordial substance according to some general principle. It is almost inconceivable that the atoms of the elements of the same group are not somehow related in structure as they are in properties. Prout's hypothesis was a forerunner, crude as it was, and in its suggestion not so far from the truth perhaps. Rowland, the physicist, is reported to have said that some day we would find that the atom was as complex as a grand piano, and that day seems to have arrived. The atom seems to be made up of an organized system of electrons, all of the same nature, each about 1/1700 as heavy as the hydrogen atom. The electron is what we call negative electricity.

At this point the theories leave the realms of chemistry and a further discussion is one of forms of force and energy, that is, physics. From our standpoint the points of interest are that the atom is complex, built up of particles of negative electricity,

electrons, in such a way that the general nature of the atom repeats itself in the different members of the same group; that the most complex systems are disintegrating with the phenomena of radioactivity. Those not now disintegrating have perhaps come from complex atoms in the past, and have arrived at a condition of stability, so that the great mass of matter, the common elements, have low atomic weights. Chemical changes, and particularly ionization, may be associated with the gain or loss of one of these electrons, with a consequent change in electric condition.

Ionization is explained by the theory of electrons as follows: When an ionogen like potassium chloride is dissolved in water, one of the electrons of the metal passes over to the nonmetal. The loss of a negative electron leaves the potassium positively charged, and the gain of this by the chlorine causes it to be negatively charged. They are now ionized. If the ions recombine, the electron resumes its normal place, and both ions cease to exist as such.

It would be a misconception to hold that this theory of the structure of the atom is a contradiction of our well established knowledge of the past, that it upsets all our preconceived notions. There is of course something startling in it, but that is because of the incomplete view of the observer, especially the layman, who often has misquoted the chemist as holding that the atom must be an indivisible unit. The ordinary atom does not change for any practical purposes, but chemists have long felt that back of the atom, as we know it, there must be some constructive material, which, built up on some regular plan, gives us distinct, yet similar elements. The idea of transmutation of one element into another

has crept in prematurely, but in a practical way is beside the mark. Comprehending the structure of the atom is one thing, our tearing it down or building it up is quite another. Such knowledge as we now possess, or hope soon to possess, is only an enrichment of the knowledge of the past, not a contradiction thereof.

ISOTOPIC AND ISOBARIC ELEMENTS

Isotopic elements may be defined as elements which have identical chemical properties, so that they fall in the same place in the periodic table, yet they have different atomic weights. The idea of isotopic elements has been developed from the study of the radioactive elements, and the finding of different atomic weights for lead obtained from different sources. (The variation is about 1.6 units.) The idea of isotopes cannot be illustrated from familiar instances, but it is proper to bring in the topic here in connection with the structure of the atom. On this assumption what we call similar, or identical, atoms, do not have absolutely the same structure, but only an approximately similar structure, with the development of identical chemical properties in each case, so far as we can determine.

Comparable with this idea is that of the isobaric elements, namely elements of equal atomic weights, but of different chemical properties. The strict illustrations are drawn from the radioactive elements, but attention may also be called to the conduct of metals like copper and iron, which, with different valences, act as though they were very different elements. Yet we say that the atom, that is the atomic weight, is the same in each.

CHAPTER XXI

GEO-CHEMISTRY

THE experiences upon which the ordinary study of chemistry is based are drawn from operations connected with material collected and applied for the common human needs, as fuel, soap, or lime. Or the material may have been even more specially segregated for the study of chemical phenomena, pure and simple. But before leaving the subject we should take a look at chemical phenomena as exhibited in the natural process of the inorganic world. That is, the chemistry of the original material of the earth's crust, the nature of the minerals making up the rocks, and of the changes taking place which result in the accumulations of the specific substances of interest. The great bulk of the earth's crust is made up of comparatively few elements, in stable and inactive combinations. This must naturally be so, as the whole drift of chemical activity is toward a stable equilibrium, and in the long periods of time which come under consideration this equilibrium will for the most part be attained. It is not surprising that substances of chemical activity should be found only exceptionally in nature. Their activity would have been satisfied sooner or later in one way or another. Men find, for the most part, these affinities satisfied, and the various substances around them in a sluggish chemical condition. The energy of the sun's rays, of water power, and that which

is stored up in coal and other fuels, furnish us means to overcome this condition of equilibrium and inactivity.

Unless the quiescent state has been overcome and new systems of chemical unequilibrium and activity established, chemical operations and industries are impossible. The chemistry of the animal and vegetable world is a field in itself. In this field there is a constant cycle of affinities satisfied and reestablished, of compounds made and unmade, of energy stored up and liberated again. The discussion of this field is left to the chapter on the chemistry of nutrition and agricultural chemistry.

The molten magma of the earth in solidifying formed the solid earth. Our attention must be confined to the outer layers of this mass, as there is no definite knowledge of the interior. The thickness of the layer which is known is ten miles or more, a comparatively meager distance. This knowledge comes from no penetration to that distance, but because through the upheavals of nature layers of the crust for such a depth have been folded and bent, and the broken edges exposed so that we may study it upon the surface. It is this mass of rock, making up the outer layers of the original material of the earth which makes the beginning of our study. Above this is the layer of secondary sedimentary rock formed from the material of the first, sediment and fragments, with the original material interpenetrating it in many outcrops. And on top of this is the uppermost layer of loose matter, sometimes of very meager depth, clay and gravel, and, what interests us most, the soil.

To some extent the general nature of all three layers, from the chemical standpoint, must be some-

what the same, as each is derived from the one below it. Here and there however, there are segregations, accumulations, concentrations, of substances radically different from the chief mass of the earth. There are formed veins and pockets of deposits of material which supply us with the salts, minerals, and ores, which are the basis of the mineral wealth of the land. The purpose of this chapter is to follow briefly the changes and their causes, which result in the modification of the original primary rock material into these deposits of special interest. There is a chemistry of the reactions by which the primary rock was formed. But this is a study beyond our scope, and we will simply begin with the primary rocks as we find them.

The chief elements of the earth's surface are these eight. Their proportions, including the sea and the air, are, according to Clarke:

	Per cent
Oxygen	50.0
Silicon	25.8
Aluminum	7.3
Iron	4.2
Calcium	3.2
Magnesium	2.1
Sodium	2.4
Potassium	2.3

We must stop for a moment to make clear the significance of the terms minerals and rocks. By mineral is meant a true chemical substance (it may be an element, but is more usually a compound), as found in nature, as part of the earth's crust. A mineral may occur in such masses that it goes to form a rock, as quartz or marble, but more frequently the rock is made up of a number of minerals, as granite, which contains the well known minerals, quartz,

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MANUFACTURE OF PHOSPHORIC ACID FROM PHOSPHATE ROCK, BUREAU OF SOILS EXPERIMENT STATION, ARLINGTON, VA.

SALT WORKS AT STAFFORD, ENGLAND—THE RESERVOIRS OF BRINE

feldspar and mica or hornblende. Chemical considerations concern only the individual minerals.

The minerals made up from the above elements are, as we would expect, salts, silicates, formed by the combination of the metallic oxides with the one nonmetallic oxide possible, namely silica. Besides silica, SiO_2, which makes up about 12 per cent of the earth's crust, the main mass of all minerals consists of silicates. The most common of these are the feldspars, $NaAlSi_3O_8$, $KAlSi_3O_8$, $CaAl_2Si_2O_8$, hornblende, (Ca,Mg,Fe) SiO_3, pyroxene, of similar composition, mica, (muscovite) $H_3KAl_3Si_3O_{12}$, all silicates differing in the relation of the oxide of silicon to the metallic oxides. In any given silicate, as feldspar, the variation of the metal changes the mineral, with no important difference in the general composition.

Silicates thus represented can account for the original form of all the more active metals, as their oxides may be included in the complex salt. With some modifications, silicates may include the nonmetals sulphur, chlorine, and boron. Apatite, a phosphate, includes phosphorus, fluorine, and chlorine. Many of the less common metals, such as copper, lead, cobalt, nickel, and zinc, are found in small amounts in these silicates, even when they are not directly apparent. Although certain information is not available, we may agree that all the elements, save carbon perhaps, have their origin in these silicates, being exceedingly thinly scattered through the rock. They have been extracted somehow, and concentrated in the deposits with which we are familiar. Without such concentration the search for them would be wellnigh hopeless.

The process by which the various elements have been removed from the primary rock, converted into certain compounds, and then deposited in the locations where we find them, is to a very great extent unknown to us. We will content ourselves with following those processes which we can understand, assuming a somewhat parallel history for the others.

Granite is a typical rock, and its constituent feldspar is a typical silicate mineral. Stable as this and other minerals seem to be, they are nevertheless subject to slow disintegration, first physical, then chemical. Changes of temperature cause rocks to crack, and the effect of the freezing of water, the wearing action of water, air, and glaciers, the disruption due to plant growth and solution in water, are all physical agencies which result in a large exposure of surface to further chemical action. To appreciate chemical action most readily, it will be convenient to assume the structure of silicates to be the union of the respective oxides. The constituent oxides have varying degrees of chemical activity and therefore are capable of separation. The prolonged action of water and carbon dioxide, that is, carbonic acid, withdraws the most active constituent and the mineral is thus disintegrated. Other active agents are the oxygen of the air which acts on ferrous compounds. It is very common to see gray rock containing ferrous iron changed to a product which is red, due the ferric iron now present. Sulphur too, in pyrites, combines with oxygen, and the sulphuric acid ultimately resulting has further disintegrating action. The juices of plants also have some chemical action, but the most important is the action of the water and carbon dioxide of the air. As a re-

sult the more active metals go into solution as carbonates, and thus start on a career of changes. Some pass on to the sea, which is the final storehouse for a number of them, but most of the potassium and calcium are intercepted and deposited on the way. That portion of the primary rock which does not pass into solution remains behind in the form of silica and clay.

The chemical decomposition of most primary rocks results in the formation of salts, soluble and insoluble, of the more active metals, sodium, potassium, calcium, and magnesium, which are found later in solution in the sea or salt lakes, or deposited by some chance in salt beds of one kind or another. Secondly, there are formed the inactive insoluble residues, like silica and clay, which may subsequently be transported to other locations or agglomerated into a secondary rock. Calcium and magnesium carbonates, at first soluble, are often later deposited in insoluble forms, and make vast masses of secondary rock.

From the above interpretation of physical and chemical changes of rock, we should have formed a picture of the secondary rock formed by changes taking place in the primary rock, and of the loose material resting on top of both, known as the soil. From all these there has been leached out, by incredibly slow processes, the two sets of mineral concentrations found in salt beds and in ore deposits.

THE SALT CONCENTRATIONS

The amount of mineral matter dissolved in surface and spring waters is usually very small, but the process has been going on for ages, and the amount thus carried away is enormous. American

rivers in the rainy regions carry 80 to 140 parts per million, about 1/100 per cent of mineral matter, one tenth of it being common salt. In arid regions the mineral content of waters is 8 to 10 times as high. Besides common salt the mineral matter consists mostly of carbonates and sulphates of calcium and magnesium, much of which is derived from secondary rocks. From the analysis of primary rocks we might expect fairly equal amounts of the four chief metals, but we notice a great dearth of potassium compounds, for they are held by the soil. Further we would naturally expect the sea to have somewhat the same composition as the waters which feed it, even if more concentrated. Here again there is a discrepancy. For neither the proportions existing in the primary rock or in the dissolving waters are found in the ocean. Here sodium predominates over all the others. The salts of the sea are about 3.5 per cent of the whole mass of the ocean, and of this four-fifths is common salt, sodium chloride. The origin of these large amounts of chlorine has never been satisfactorily explained.

As has already been implied, the salt deposits which we know were formed in all probability by the evaporation of landlocked bodies of sea water. Some of these are so vast that we must assume a frequent replenishing of the brine, and consequent accumulation of the salts. Sodium chloride, common salt, is of course the most conspicuous mineral of these deposits. But in the famous Stassfurt deposits the potassium and magnesium salts are also still to be found.

It might be assumed that all sorts of compounds must have found their way into the sea, and should be found there with sufficient searching. This can

be true however, to only a limited extent, as so many of the metals, for example, are likely to form insoluble compounds through interaction with other substances with which they come in contact, and to be deposited rather promptly. Yet a number of elements are found indirectly, as iodine in the ash of seaweed. The perennial interest in gold in sea water is based upon considerations such as these.

The salt deposits of desert regions (alkali) have a history similar to that of the salts of the sea. But they come from restricted sources and their composition is not the same. The presence of sodium carbonate and of sodium borate (borax) are conspicuous variations from the composition of sea-water deposits. Another familiar deviation is that of the sodium nitrate beds of northern Chile.

ORE DEPOSITS

From what has already been stated it must be evident that ore deposits of the less abundant metals are concentrations of material which has previously been highly diffused, so highly diffused in fact that it may not in many cases be traced to its original location. The meaning of the word "ore" is based upon practical values. It usually means an accumulation of a metal or its compound (applied mainly to the heavy metals) of such a character that the extraction of the metals therefrom is profitable. Ordinary yellow sand contains more iron than there is of metal in a rich gold ore, yet in the one little attention is given to the iron content, while the other is of great value. Iron ore should contain about 50 per cent of iron to pay for its extraction, while a gold ore may be profitable with a gold content of 1/200 per cent. It is a question of economics,

not of chemistry. In a remote region where transportation is difficult and supplies costly, there must be a larger return than where the outlay is less. The market value of silver determines whether the silver mines of Nevada are to be worked or not.

The ores of the ordinary metals may contain the metal either as the free or native metal, or in some form of compound. Evidently only the less active metals will be found free in any amount, for the rest would in time have asserted their activity and formed some kind of combination. Referring to the electromotive list, it may be observed that only the metals below hydrogen are found free. Sulphides are abundant as are also the oxides, hydroxides and carbonates. In fact, these five forms include 90 per cent of all ores. Metals occur also as chlorides, as silicates, and in combination with arsenic. Gold, copper, and platinum are important free metals. Silver, mercury, copper, lead, arsenic, antimony, zinc, cobalt, and nickel occur as sulphides; copper, iron, aluminium, manganese, and zinc have important oxides. Pyrites, FeS_2, though exceedingly abundant, hardly ranks as an ore of iron, on account of the difficulty of extracting the iron in sufficiently pure form. It does, however, rank as an ore of sulphur and is used extensively for the making of sulphuric acid.

How were the metals removed from their original combinations, transported, and deposited in the places and forms in which they are found? The first answer is this: It is likely that now and then the conditions of cooling of the molten mass of the earth resulted in some partial concentration of one or the other of the heavy metals free or combined. From such incipient concentrations the action of

water caused them to go into solution. In such cases water may have acted under very unusual conditions. The temperature and pressure may have been very high and the water may have contained carbon dioxide, alkalis, or even acid from the products of oxidation of sulphur compounds. The periods of time involved were very long, and no matter how slow the action it may yet have been complete. In the rocks, primary or secondary, there developed fissures, as the result of geological changes, cooling, drying, shrinking, and folding of rocks, with subsequent extension by erosion and solution. Now the compounds of the metals carried in solution traversed these openings and the conditions of solution changed. There was alteration in the pressure, temperature, evaporation of the solvent, loss of carbon dioxide, or there was contact with other substances and solutions which exerted a chemical action. As a result of these changing conditions the compounds previously held in solution were deposited. The deposits are not solely of the valuable ores. The greater portion may be useless material, the gangue material through which the ore is scattered in one form or another. The most abundant gangue minerals are quartz, SiO_2, calcite, $CaCO_3$, barite, $BaSO_4$, fluorspar, CaF_2, and a number of silicates. Although this explanation assumes long periods of time, there are cases in abundance under observation showing the solution, concentration, and redeposition of ores in short periods of time. Deposits so formed may be subject to a second concentration, by either physical or chemical processes. Or they may be modified chemically, the upper layers of lead sulphide, for example, are sometimes converted into lead sulphate and car-

bonate by the action of the oxygen and carbon dioxide of the atmosphere. Ore deposits are not necessarily in the form just described. Other conditions may result in beds of ore, or in impregnations of permeable rock.

MINERALOGY AND CRYSTALLOGRAPHY

Minerals have been defined in a former paragraph as individual chemical substances, sometimes elements, more often compounds, as they are found in nature. They are the units of which the rocks are built and they are the starting points for any consideration of chemical changes.

From even a brief study of the minerals, it may be seen that they fall into two groups, the first that of the silicates and their modifications, which go to make up the mass of the primary rock; the second that of minerals of a very different chemical composition, made up in great measure of modifications and extractions from the first. The total number of species identified is about one thousand, one hundred being somewhat common forms. Of these last about half belong to the first class, the silicates, and the rest to the other class. Each group has its own features of interest. In the first group the geologist finds a greater interest than does the chemist, for in them he finds the interesting evidence for his study of the history of the earth. In the second group are the more reactive substances which, through chemical manipulation, become of service to men. The German expression, "aufschliessen," to unlock, as applied to the silicates, is very suggestive. It is no easy matter to pass from most of the silicates to the compounds of the other type. Witness the vast amounts of

potash locked up in the feldspar of granite rocks, while the only forms which are available to us are those which, through the slowly acting operations of nature, have been segregated from the original rock and concentrated in secondary deposits.

The identification of minerals is accomplished by the study of their physical and chemical properties. The latter applies to only a limited extent to the many silicates, as they are too inactive, but with the help of the blowpipe much can be accomplished with the minerals of the second group. The presence of sulphur and arsenic is determined by the odor of their oxides. Halogen acids are easily liberated and identified. Carbon dioxide is easily detected, and other chemical tests, not differing from the usual tests of qualitative analysis are useful in establishing their nature.

The physical properties which are of use are: luster; color, both of the mass and of the powder; hardness; malleability; nature of the fracture, which is cleavage when it follows the lines of crystallization; fusibility; specific gravity; optical properties; and especially crystalline form.

The luster is described as metallic, vitreous, resinous, dull, and otherwise. Superficial as it may seem, it gives a very prompt clue to the nature of a mineral. The metals and some of their sulphides and oxides have such a pronounced metallic appearance that they may be distinguished with great certainty from the more stony or glassy materials of other composition. The color is often characteristic, due to the nature of the mineral itself, or to rather consistent impurities. Of special interest is the color of the powder obtained most easily by

making a "streak," that is, rubbing the mineral against a rough porcelain surface. The material rubbed off as a powder gives the desired information.

Hardness is determined by comparison with a fixed scale of accepted minerals.

Malleability serves to distinguish with certainty between a metal and a compound. A few compounds are so metallic in appearance that they are deceiving. Their conduct under the hammer shows whether the specimen is a metal or not.

Minerals often break with a fracture which is characteristic and instructive. Most important in this connection is the fact that in many crystals or crystalline masses there are predetermined lines along which the fracture will take place. This is the cleavage, and when it does apply is readily recognized. Cleavage has the appearance of the regular breaking of a lump of cannel coal when placed upon the fire, but the latter is not due to crystalline structure.

Fusibility, like hardness, is determined by comparison with a fixed scale. The specimen, in the form of a thin fragment, is heated in the blowpipe flame and from the readiness of the melting the number representing the fusibility is assigned.

Specific gravity is determined in the regular way by comparing its weight in water and out of water. With respect to specific gravity there is again a rather sharp distinction between different classes of minerals, as there is between the two great classes of metals, the heavy and the light. The simple compounds of the heavy metals, when they occur as minerals, usually have a specific gravity of five or above, while the other minerals, particularly the silicates, have a specific gravity of from 2.5-3.

Within narrower limits the determination of this property gives more exact data.

Crystalline form. The crystal form is one of the most important features connected with the appearance and structure of matter. Most men have a vague idea of a crystal as being a glassy, geometric solid. But the mineralogist has reduced the study of crystalline forms to a mathematical science. A piece of glass cut out in a proper shape is, of course, not a crystal. The external crystal form must represent an internal arrangement of the molecules, and although the relation of crystalline form to chemical structure is a subject not yet worked out to any degree of completion, the mineralogist has applied the matter satisfactorily in a descriptive way.

A true crystal is bounded by plane faces, with no reentrant angles. Although the faces are the most conspicuous, that which really determines the crystal form is the angle which the faces make with each other. On this interpretation, using a homely illustration, all ordinary boxes with squared edges and right angles would represent the same crystal form, whether they were perfect cubes or elongated in one direction or another or were large or small. Fortunately, in any given case one kind of crystal usually assumes more or less the same form, and so the matter is in practice less complicated. The angles are measured with great accuracy by means of a goniometer, and from them the crystal form calculated by methods by no means simple. For ordinary practice, the crystal forms are usually readily apparent to the trained crystallographer, and he can use this knowledge for the solution of his problems.

CHAPTER XXII

ORGANIC CHEMISTRY

ALTHOUGH, by strict interpretation, Organic Chemistry should be considered a chapter of General Chemistry, strong reasons stand out for studying the subject by itself. In the first place, the compounds involved, made up predominantly of carbon, hydrogen, oxygen, and nitrogen, number so many that no other set of compounds is comparable with them; secondly, the reactions and principles of organic chemistry are sufficiently distinctive to require special attention; and, finally, the subject matter is concerned to a considerable extent with the products of living organisms. The last of these accounts for the name which has been criticized as being too exclusive. Another name, "the chemistry of the hydrocarbons and their derivatives," is cumbrous, but exceedingly suggestive, and we will keep this suggestion continually before us.

From a practical standpoint the subject matter of organic chemistry might be considered as mainly included in two groups, one consisting of natural and the other of artificial products. In the former are all the substances formed by animal or vegetable organisms or those derived from them in simple ways, while in the latter are the products formed by the more elaborate manufacturing processes, proceeding from such raw materials as coal tar. The first group includes the rather complex compounds

associated with the chemistry of living things, namely, biochemistry; the constituents of foods; the products obtained by fermentation processes; the substances involved in the extensive fat and oil industries; the essential oils, including perfumes and flavors; many medicinal preparations; and, lastly, the textiles, which may include cotton, silk, wool, leather, and rubber. The artificial group concerns itself with such substances as are obtained from the destructive distillation products of wood and coal, most conspicuous among which are the much discussed coal-tar products, particularly the dyes. Explosives, photographic chemicals and synthetic drugs are included in this group. Petroleum forms an additional group by itself.

The compounds which come within the range of the study of organic chemistry are very many. Their number is in the hundreds of thousands, and acquaintance with most of them as individuals is impossible. We must develop the principles underlying the subject and the thread of argument running through them all. The definition used above, "organic chemistry is the study of the hydrocarbons and their derivatives," is the first main principle to be established. We must first inquire, then, as to the nature of the hydrocarbons. When we have studied these, we will have established a basis from which we may depart for the derivation of all the other compounds of our subject.

A hydrocarbon is a compound composed of carbon and hydrogen only. Carbon is outstanding in its power to build up complex molecules, one atom adding itself to another to an extent unknown for other elements. The valences not applied for linking the carbon atoms together are filled out with hydrogen,

and the result is a hydrocarbon. Typical illustrations are methane, CH_4, ethane C_2H_6, benzene C_6H_6. There are about a thousand such combinations, which may seem an appalling number for our very beginning. We may, however, simplify this matter promptly by saying that all these hydrocarbons fall into two main groups, the paraffin group and the benzene group. The hydrocarbons of both groups have many points of resemblance. They are all combustible, and not very reactive, light, insoluble in water. Two points of difference show themselves. The first of these is illustrated by the comparison between the formulæ C_6H_{14}, hexane, of the one group, and C_6H_6, benzene, of the other. In the former case, the six carbon atoms are loaded with all the hydrogen atoms which they theoretically can hold. So we say the paraffins are saturated. The latter, then, is evidently unsaturated, for it has many hydrogens less than the theoretical possibility. A second point of difference is that indicated by the name paraffin, meaning little affinity. The hydrocarbons react very little with acids, while sulphuric and nitric acids attack the benzenes somewhat readily. This demarcation is fairly thorough, and the classification determined thereby is usually taken as the basis of the study of organic chemistry.

THE PARAFFIN HYDROCARBONS

The hydrocarbons which are found to belong to this group contain varying amounts of carbon and corresponding amounts of hydrogen. We would naturally consider these in the order of their carbon content, and in doing so find that they may be arranged in a regular series. Thus arranged, it will be noted their carbon and hydrogen content increases regularly. It

will be profitable to consider a table showing names, formulæ, and properties of these hydrocarbons.

THE PARAFFIN HYDROCARBONS

Formula of hydrocarbon	Boiling point C.	Specific gravity	Melting point, C.
CH_4	gas	....	..
C_2H_6	gas	....	..
C_3H_8	gas	....	..
C_4H_{10}	1°	....	..
C_5H_{12}	36°	0.628	..
C_6H_{14}	69°	0.658	..
C_7H_{16}	98°	0.684	..
C_8H_{18}	125°	0.708	..
C_9H_{20}	149°	0.718	..
$C_{10}H_{22}$	173°	0.730	..
$C_{11}H_{24}$	195°	0.741	..
$C_{12}H_{26}$	214°	0.751	..
$C_{13}H_{28}$	234°	0.757	..
$C_{14}H_{30}$	253°	0.764	5°
$C_{15}H_{32}$	270°	0.769	10°
$C_{16}H_{34}$	287°	0.773	20°
$C_{17}H_{36}$	303°	0.778	23°
$C_{18}H_{38}$	317°	0.784	28°

A study of this table reveals many of the significant points of this series and is indicative of what we will find in all series of organic compounds. The increase in molecular complexity is regular, and the physical state follows directly upon this. The first of the series is a light gas, and as we move along the tendency to become a liquid is greater. The higher members of the series are liquids, but very volatile. Then come less volatile liquids, and finally solids. The specific gravity increases regularly, and other properties which can be measured vary similarly.

In those respects in which the paraffin hydrocarbons do not vary with the regularity just emphasized, they are remarkably alike. They are insoluble in water, combustible, and are not readily reacted upon by acids and other substances. Derivatives are

practically never obtained from them directly except for scientific studies. Their use is confined to those fields with which we are familiar as parts of the petroleum industry, namely combustibles and lubricants, uses not associated with any peculiar chemical reactivity.

Before the derivatives of the paraffins are taken up, it will be desirable to touch upon a chapter of applied organic chemistry which to this day of gas engines is of such vital interest, namely petroleum and its products. Crude petroleum, and for this discussion natural gas may be included, is a naturally occurring mixture of the different members of the paraffin series. The great value of petroleum lies primarily in its combustibility; but the various phases of the industry are determined by the varying physical properties of the different members of the series. The first members are gases, and for some purposes gas is an ideal fuel. Next comes the mixture of members which we may call gasoline, a liquid, easily transported and handled, yet so readily converted to a gas, when wanted in that state, that it is altogether suited for use in a gas engine. The next group may be called kerosene, too little volatile for ordinary gas engines, but by means of certain expedients (the wick is one of them) converted into a gas and burned for light and heat. Another higher group is represented by the lubricating oils, possessing physical properties suitable for such purposes. Finally we have paraffin, made up of solid members, useful just because they are solids. Some years ago, before the uses of petroleum products were so definitely concentrated in the above groups, there were various intermediate groups, for example, between gasoline and kerosene, not quite

suitable for either, hence put to the humble use of cleaning liquids. Another group was called burning oils, being a residue not suited to other needs. The whole tendency now is to concentrate into groups which have the greatest value, and particularly gasoline. The major portion of petroleum refining is the mechanical separation of a mixture of many individual hydrocarbons into convenient parts, no one part being a pure substance, but made up of neighboring members of the series, nearly enough alike to serve the same purpose. The most highly esteemed is gasoline, which, interestingly enough, in the early days of oil refining was a drug on the market. Now the great demand for this commodity has led refiners to include neighbors of the series so far down in the list that their tendency to become gaseous is appreciably less than that of the gasoline of some years ago. This has been rendered possible by the increasing mechanical perfection of the automobile engine. Now that men have enjoyed the gratification of two great human aspirations, the automobile and the flying machine, it is unlikely that they will allow the exhaustion of the petroleum supply in the future to put an end to these pleasures. In what direction they will turn successfully for a motor fuel it is not yet possible to say. Alcohol, being obtained from the fermentation of vegetable products, can always be supplied, if it fills the need satisfactorily. Coal tar hydrocarbons, obtained from the coke-making operations, may help somewhat, but the amount obtained does not promise to be adequate. Certain bituminous shales, upon destructive distillation, yield hydrocarbons and promise somewhat for the future. It would be interesting if the petroleum industry, which made its beginnings in

these shales, should in time revert to them for its chief supply of raw material.

PARAFFIN DERIVATIVES

The derivatives of the hydrocarbons are related to the hydrocarbons in that in place of one or more of the hydrogen atoms we find other elements or groups. The three most important groups which replace the hydrogen are chlorine, the hydroxyl group, —OH, and the amino group, $-NH_2$. From these three groups are developed almost all the interesting derivatives of the paraffin series, not always in the simplest form nor always readily recognizable. These derivatives are nevertheless always thus related, and with sufficient study the relationship becomes apparent.

A list of such compounds shows the scope of the subject:

Original hydrocarbon	Halogen derivative	Hydroxyl derivative	Amino derivative	Double halogen derivative
CH_4 methane	CH_3Cl methyl chloride	CH_3OH methyl alcohol	CH_3NH_2 methyl amine	CH_2Cl_2 dichlor methane
C_2H_6 ethane	C_2H_5Cl ethyl chloride	C_2H_5OH ethyl alcohol	$C_2H_5NH_2$ ethyl amine	$C_2H_4Cl_2$ dichlor ethane
C_3H_8 propane	C_3H_7Cl propyl chloride	C_3H_7OH propyl alcohol	$C_3H_7NH_2$ propyl amine	$C_3H_6Cl_2$ dichlor propane
C_4H_{10} butane	C_4H_9Cl butyl chloride	C_4H_9OH butyl alcohol	$C_4H_9NH_2$ butyl amine	$C_4H_8Cl_2$ dichlor butane
C_5H_{12} pentane	$C_5H_{11}Cl$ pentyl chloride	$C_5H_{11}OH$ pentyl alcohol (amyl alcohol)	$C_5H_{11}NH_2$ pentyl amine	$C_5H_{10}Cl_2$ dichlor pentane

and so on, through the whole list of hydrocarbons.

This table includes only the simplest and most direct compounds. Each set of derivatives represents a series, directly comparable with the original hydrocarbon series and, like that series, showing regular progression in physical properties.

Now another principle of organic chemistry may be added to the principles already enunciated. It is this: When a certain group, for example, chlorine, is present, it may be removed and replaced by one of the others. The interchange of groups is one of the most useful of organic reactions. It enables us to pass from one type of compound to another, more or less at our pleasure. It is often true that a given compound cannot, for one reason or another, be directly prepared. It is only necessary to select another compound of similar type, and then to pass over, so to speak, to the one we wish. For example, $C_2H_6 \rightarrow C_2H_4(OH)_2$ cannot be accomplished. $C_2H_6 \rightarrow C_2H_4Cl_2 \rightarrow C_2H_4(OH)_2$ can be accomplished, and thus indirectly we have gained our end. Without this device the practical possibilities of organic chemistry would have many limitations, for after all, organic compounds are not conspicuously reactive, and combinations must be effected by whatever favoring conditions we can apply.

HALOGEN DERIVATIVES

The chlorine, or more generally, the halogen, derivatives may be considered briefly as a whole. We have a long list of compounds, for we have several principles of variation, namely, by introducing chlorine, bromine, or iodine; by introducing one or more atoms of these; or by deriving them from the different original hydrocarbons. Formulæ representing these three variations are, CH_3Cl, CH_3Br, CH_3I;

secondly, CH_3Cl, CH_2Cl_2, $CHCl_3$ CCl_4, and lastly CH_3Cl, C_2H_5Cl, C_3H_7Cl. The halogen derivatives, represented by the familiar chloroform, are colorless substances of sweet ethereal odor, and are gaseous, liquids, or solids according to their composition. They are insoluble in water, and of a high specific gravity, some of the liquids being three times as heavy as water. Some have economic application, as chloroform and the corresponding iodoform. Carbon tetrachloride, CCl_4, not being combustible, is used in fire extinguishers, as it is volatile enough to penetrate into odd corners and thus to exclude the air from the burning substance.

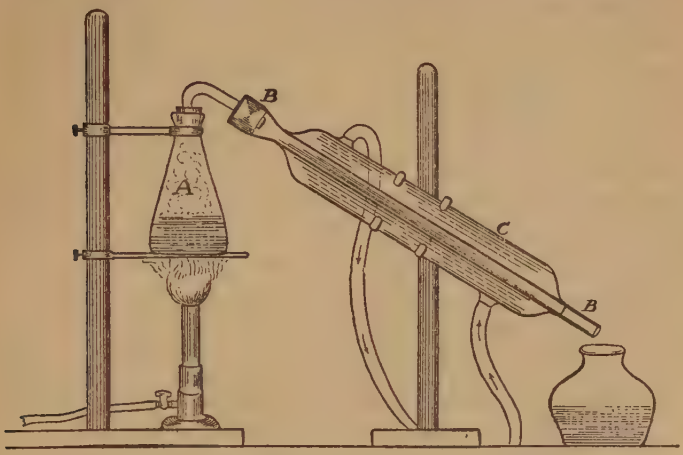
HYDROXYL DERIVATIVES, OR ALCOHOLS

This is probably the most important class of derivatives of organic chemistry. It must be noted that the alcohols contain a water residue, the —OH group; hence the alcohols are similar to water in many respects. They form a regular series, in which the properties vary regularly. It will be advantageous to look more closely at this series.

CH_3OH, Methyl alcohol. Liquid boiling at 66°C.
C_2H_5OH, Ethyl alcohol. Liquid boiling at 78°C.
C_3H_7OH, Propyl alcohol. Liquid boiling at 97°C.
C_4H_9OH, Butyl alcohol. Liquid boiling at 117°C.
$C_5H_{11}OH$, Amyl alcohol. Liquid boiling at 137°C.
$C_{16}H_{33}OH$, Hexadecyl alcohol. Solid.
$C_{18}H_{37}OH$, Octadecyl alcohol. Solid.

Alcohols as a Class.—The first of the alcohols mentioned have a pleasant odor, familiar from pure ethyl or grain alcohol. A number beginning with C_4H_9OH have the irritating odor of fusel oils. The highest alcohols, being nonvolatile solids, possess no odor. The first members of the series, on account of

the presence of the hydroxyl group, are soluble in water, but this solubility is less for higher members and the highest members are altogether insoluble, as the influence of the hydroxyl group is lost. Like most organic compounds they are combustible. Chemically their most important property is due to



APPARATUS FOR THE DISTILLATION OF LIQUIDS, USED FREQUENTLY IN ORGANIC MANIPULATIONS

The liquid, or mixture of liquids, is boiled in A, and the vapors escaping are cooled in the tube B, which is surrounded by the water jacket C, through which a stream of cold water is passed. The condensed liquid is collected in the receiver, which is changed as the different ingredients of the mixture in A pass over.

their resemblance to sodium hydroxide, NaOH; they act as weak bases, and so form salts.

Some of the individual alcohols are so important in various relations that they must be discussed in some detail. The first of these is ethyl, or grain alcohol, spirits of wine, C_2H_5OH. This alcohol is obtained, as is well known, by the fermentation of sugar, or of substances like starch,

which are converted into sugar. The reaction is represented by the equation, $C_6H_{12}O_6$ (upon fermenting) $\rightarrow 2CO_2 + 2C_2H_5OH$. No other way of preparation is of any note. Ethyl alcohol boils at 78° C. (172° F.), and is somewhat lighter than water. The properties to which men give most weight are its combustibility, its solvent action, and its physiological action, to which might be added a growing tendency to use it as a raw material for the manufacture of other organic substances.

Methyl alcohol, called wood alcohol, because it is obtained by the destructive distillation of wood, resembles ethyl alcohol very closely, but is peculiarly poisonous. Because of the resemblance, especially when pure, mistakes are frequent, and hence cases of poisoning are common. Aside from this poisonous action, wood alcohol has properties very similar to those of ordinary alcohol. However, it should be used with care as the action of poisons is not limited to their introduction into the stomach.

Some of the higher alcohols are formed in small amounts during the fermentation process by which ethyl alcohol is prepared. They are obtained commercially in this way and amyl alcohol in particular is useful as a solvent, especially when combined with acetic acid to form "banana oil." These alcohols, known as fusel oils, are of disagreeable odor and of harmful physiological effect. Some of the highest alcohols are solids, and of great importance in biochemistry.

THE AMINES

The third class of derivatives of the hydrocarbons is the class of amines, of which methylamine, CH_3NH_2, ethylamine, $C_2H_5NH_2$, and propylamine, $C_3H_7NH_2$, are examples. This amino group is de-

rived from ammonia, and consequently these amines have properties very similar to those of ammonia. They differ most markedly in their ready combustibility, a property which ammonia lacks. The simple amines are of minor importance, but in their complicated forms they include the ptomaines, the proteins, and many products of metabolism, such as uric acid and urea. These compounds, built up from amines, have a rather complicated structure, but may always be referred back to this type of compound.

THE DOUBLE AND TRIPLE ALCOHOLS

Our ordinary conception of an alcohol is that of a hydrocarbon one of whose hydrogen atoms is replaced by hydroxyl. Now when a hydrocarbon molecule contains several carbon atoms, this condition may be repeated for each of the carbon atoms, with the result which may be called a double or triple alcohol. We will pass on at once to the triple alcohol, as this exceeds all the others in interest. It is derived from propane, and contains three hydroxyl groups, one for each carbon, $C_3H_5(OH)_3$. This is ordinary glycerine, the name being given on account of its sweet taste. Glycerine has certain medicinal and industrial uses, but its chief interest lies in its relation to the fats and to nitroglycerine. In each case the alcohol character of the glycerine asserts itself and it acts as a base. Other so-called polyhydroxy-alcohols exist, and the one with six carbons, mannite, is very suggestive of the sugars, which are closely related. It has the same crystalline appearance and a somewhat sweet taste. All these complex alcohols are very soluble in water, as might be expected from the numerous hydroxyl groups.

OTHER OXYGEN DERIVATIVES—ETHERS, ALDEHYDES, ACIDS, AND ESTERS

Besides the alcohols there are four other classes of oxygen derivatives which play so great a rôle among organic compounds that their composition and properties need attention, even if the points involved may seem somewhat obscure. These four classes are the ethers, the aldehydes, the acids, and the esters, each in its turn formed by a modification of the alcohol. This will be explained in the sequel.

Ethers.—Ethers are modifications of the alcohols obtained by splitting off water from two alcohol molecules. The hydrocarbon group of the alcohol and its relation to the oxygen are not changed. We may say that ether is an oxide while alcohol is a hydroxide. There is an ether corresponding to every alcohol, but ethyl ether is the most common and the one usually indicated by the name. The ether structure may also be considered from the following standpoint. Beginning with water, H — O — H, we replace one hydrogen by means of the ethyl residue and obtain C_2H_5 — O — H, ethyl alcohol. Replacing the second hydrogen gives us C_2H_5 — O — C_2H_5, or ethyl ether. The two ethyl groups are evidently held together by means of the oxygen atom. Ordinary ether is very volatile and inflammable. Its bad reputation in respect to explosiveness is due to the readiness with which the gas passes off, and the likelihood of its becoming ignited at a neighboring flame. Hence, before handling ether, all neighboring lights should first be extinguished. Ether is not explosive. It is simply likely to form an explosive mixture with air. Ether is a very light liquid and only slightly soluble in water. Chemically it is

rather inactive. Its chief use is as a solvent and an anæsthetic. In respect to solvent action we have in water, alcohol, and ether, an interesting group. Water is the typical inorganic liquid, and hence is the best solvent for inorganic compounds. Ether, on the other hand, represents the same relation to the organic compounds, while alcohol, partaking of the nature of each, has intermediate solvent properties.

More important than the particular characteristics of ordinary ether is the structure of its molecule, the ether structure. By this is meant the splitting of water from two alcohol groups $\begin{matrix} C_2H_5OH \\ C_2H_5OH \end{matrix}$ and the consequent formation of $\begin{matrix} C_2H_5 \\ C_2H_5 \end{matrix}\!\!\searrow\!\!\swarrow O$, or $C_2H_5 - O - C_2H_5$. The two hydrocarbon residues of the two alcohol molecules have become linked together by means of the oxygen. This linking must be looked at in the light of a separation, so that the two units always preserve their individuality. If the formula for ether were written $C_4H_{10}O$, we might lose sight of that fact. Written $C_2H_5 - O - C_2H_5$ we are reminded of the two facts, first that ether is obtained from ethyl alcohol, $C_2H_5OH + C_2H_5OH \rightarrow HOH + C_2H_5OC_2H_5$, and further of the fact that this process can be reversed, and ether reconverted into its simpler constituents $C_2H_5 - O - C_2H_5 + HOH \rightarrow C_2H_5OH + C_2H_5OH$. This latter process is called hydrolysis, meaning breaking apart by the addition of water. The reaction is one of the most important of both branches of chemistry. The three nutrients, the carbohydrates, the fats, the proteins, are complexes held together somewhat on this order, and in their upbuilding and utilization as foods the above linking

and unlinking are processes repeated with the utmost frequency.

In trying to appreciate the structure of the next two groups, a schematic representation of their relation to alcohol will be helpful. Ethyl alcohol has the formula, C_2H_5OH. It may be written $CH_3.CH_2OH$, or better for our purpose $CH_3—C\begin{matrix}\diagup OH\\ —H\\ \diagdown H\end{matrix}$, this last device being for the sake of emphasizing the fact that one of the three hydrogen atoms of the second group is replaced by a hydroxyl group. $CH_3.C\begin{matrix}\diagup OH,\\ —OH,\\ \diagdown H\end{matrix}$ and $CH_3.C\begin{matrix}\diagup OH\\ —OH\\ \diagdown OH\end{matrix}$ are formulæ which would naturally be suggested by this idea. And such compounds should normally exist. But it is found to be true that as soon as two hydroxyl groups are linked to one carbon, water splits off; thus, $CH_3.C\begin{matrix}—|OH\\ —\overline{O}|H\\ —H\end{matrix}$ and $CH_3.C\begin{matrix}—|OH\\ —\overline{O}|H,\\ —OH\end{matrix}$ and there remain the compounds $CH_3.C\begin{matrix}=O\\ \diagdown H\end{matrix}$ and $CH_3.C\begin{matrix}=O\\ \diagdown OH\end{matrix}$ as the actual representatives of the above. We have then in these three compounds, the alcohol, the aldehyde, and the acid, the logical results obtained by the attaching of one, two, or three hydroxyl groups to one carbon, $CH_3C\begin{matrix}\diagup OH\\ —H\\ \diagdown H\end{matrix}$, $CH_3C\begin{matrix}=O,\\ \diagdown H\end{matrix}$ $CH_3.C\begin{matrix}=O.\\ \diagdown OH\end{matrix}$ The well-known illustration is the conversion of ethyl alcohol to acetic acid when cider turns to vinegar, the oxidizing action of air being essential to the change.

Aldehydes. We are now ready for a brief examination of the nature of the aldehydes. As in the case of all other derivatives, there is at least one for every hydrocarbon. Only one needs to be mentioned in addition to the acetic aldehyde mentioned above. That is formaldehyde $H.C\begin{matrix}\diagup\!\!\!\diagup O \\ - H\end{matrix}$, derived from methane. The aldehydes hold an intermediate place between the alcohols and acids, and show a great instability, tending to gain hydrogen, thus reverting to the alcohols, or to gain oxygen, thus passing on to the acids. They unite readily with various other active substances. The molecules even tend to unite with each other, and to form more complex molecules, which may be again converted into the simple form. Such building up is called polymerization, and may involve two or more simple units. Formaldehyde acts as a disinfectant, for reasons probably connected with its high reactivity. It has the same proportionate composition as the carbohydrates, CH_2O, as compared with $C_6H_{12}O_6$, the formula for glucose. It is likely that the building up of the carbohydrates in the process of plant growth is through the polymerization of formaldehyde, which in its turn has been formed from carbon dioxide (carbonic acid). $CO_2 \rightarrow H_2CO_3 \rightarrow CH_2O \rightarrow C_6H_{12}O_6$. The aldehyde group $-C\begin{matrix}=O \\ \diagdown H\end{matrix}$ recurs very frequently, and is particularly important in the sugars.

Acids. The third member of the sequence is the acid. All real organic acids contain the group $-C\begin{matrix}=O \\ \diagdown OH\end{matrix}$, which represents the third oxygen product. As this group may be part of all sorts of organic compounds, the number of possible acids is very

great. Our discussion now involves only the acids of the regular structure, involving no other feature besides. Acids are obtained, as are the other derivatives, at least one from every hydrocarbon.

THE SERIES OF FATTY ACIDS

		Boiling Point
$H.CO_2H$	Formic	99°
CH_3CO_2H	Acetic	118°
$C_2H_5.CO_2H$	Propionic	141°
$C_3H_7.CO_2H$	Butyric	163°
$C_4H_9CO_2H$	Valeric	186°
$C_5H_{11}.CO_2H$	Caproic	205°
$C_{15}H_{31}CO_2H$	Palmitic	solid
$C_{17}H_{35}CO_2H$	Stearic	solid

The acid nature of these is due to the oxidized condition of the nonmetal carbon. They are in this respect not dissimilar to the inorganic acids. The acid groups, CO_2H, NO_3H, SO_4H_2, PO_4H_3 are altogether comparable.

The first three of these acids are typified by the well known acetic acid, the acid of vinegar, which is about 4 per cent acetic acid. It is a colorless liquid of sharp sour smell and taste, very soluble in water. Although it is a strong acid when considered as a constituent of foods, it is, when considered purely chemically, only about 1/100 as strong as hydrochloric acid. The group of acids containing from four to six carbon atoms are substances of an unpleasant rancid odor. In the higher acids, the peculiar acid carboxyl group, $—CO_2H$, is of such comparatively minor importance that these acids are insoluble, fatlike solids, with no marked odors. Yet they are real acids, for they form salts of various kinds. The salts formed with the triple alcohol glycerine as a base include the highly important group of substances called fats, while the

salts which they form with sodium constitute soap.

Esters.—Parallel with the group of organic acids, is a group of compounds the nature of which might be anticipated. These are the salts, or esters, of the organic acids, formed with the alcohols, which are bases. These esters are many in number, being made up in great variety from the various alcohols and the various acids. Ethyl acetate, $C_2H_5.OCOCH_3$, is a typical member. Amyl acetate is another, $C_5H_{11}.OCOCH_3$, and is the substance which gives the banana its flavor and odor. These esters have a pleasant fruity odor, and many of the flavors of fruits are due to their presence. They are very useful solvents, and so-called banana oil is much used for this purpose. Another set of these salts is found in the waxes. These are made up of higher alcohols and acids. Beeswax is $C_{30}H_{61}.OCOC_{15}H_{31}$. Still more important are the fats, which are made up of glycerine as the base, and any one, or several, of the higher fatty acids as the acid. A typical fat is $C_3H_5(OCO.C_{17}H_{35})_3$, which might be written for the sake of simplification, Gl $(St)_3$. This is glyceryl stearate. The acid group may be replaced by a variety of other acids, but the most commonly occurring are stearic acid, and two others, palmitic acid, $C_{15}H_{31}.CO_2H$, and oleic acid, $C_{17}H_{33}CO_2H$. When the fatty acid is split off by means of sodium hydroxide, and thus united to the sodium, soap is formed, $NaOCO.C_{17}H_{35}$, sodium stearate. This process of soap-making, called saponification, is represented thus:

$C_3H_5(OCO.C_{17}H_{35})_3$ the fat, $+ 3NaOH$ (lye) $\rightarrow 3NaOCOC_{17}H_{35}$ (soap) $+ C_3H_5(OH)_3$ glycerine; or more simply thus: Gl $(St)_3$, fat, $+ 3Na\ OH \rightarrow$ Gl $(OH)_3$, glycerine, $+ 3Na$ St, soap.

THE MORE COMPLEX DERIVATIVES

Our study has given us a glimpse of the more important simpler derivatives of the paraffin series. Many ordinary useful substances are comprehended within this list; yet many have not been mentioned. The well-known vegetable acids, the carbohydrates, the many substances containing nitrogen associated with the animal organisms are more complex, and will now be considered. Although more complex, no fundamentally new ideas will be developed. These more complex substances are derived by repetitions or modifications of types of derivations already established. The final result is perhaps by no means simple, yet simple ideas underlie the formation of all these compounds.

Besides acetic acid, five other acids come into frequent discussion in connection with our foods and other ordinary substances. These acids are oxalic, lactic, malic, tartaric, and citric acids. Of these, lactic acid is usually handled as a sirupy liquid containing water, while the others are well known in crystallized form. The formula of oxalic acid is $CO_2H.CO_2H$; compare acetic acid $CH_3.CO_2H$, and ethane $CH_3.CH_3$. It is therefore the same as acetic acid with the hydrocarbon residue therein converted to an acid residue. Oxalic acid occurs in certain sour plants, oxalis and rhubarb. All these acids in concentrated form are poisonous owing to their chemical activity, but as we meet with them in foods they are highly diluted. Oxalic acid is perhaps especially dangerous on account of its action in precipitating (making insoluble) the calcium necessary for life processes. Malic acid, $C_2H_3.OH.(CO_2H)_2$, and tartaric acid, $C_2H_2(OH)_2\ (CO_2H)_2$, are closely re-

lated. They are both, as can be seen, double acids, and in addition include respectively one and two alcohol groups. In comparison with the very pronounced properties of the acid groups present, these alcohol groups are very inconspicuous. Citric acid is on the same order, but more complex, $C_3H_4.OH.(CO_2H)_3$, a triple acid with one added alcohol group. These acids are the acids respectively of fruits like the apple, the grape, and the citrus-fruits. The last two are obtained commercially, and tartaric acid is used in large amounts in the preparation of baking powders. Lactic acid is the acid developed in the souring of milk, and sourness of bread is due to this also. Its formula is $CH_3CHOH.CO_2H$, namely, propionic acid, modified by the presence of an alcohol group. There are many other acids of this double or mixed nature, but these common members of the group will serve for sufficient illustrations.

CARBOHYDRATES

The term carbohydrate is applied to a group of substances, the sugars, starches, gums, and cellulose, which are intimately associated. The name, meaning carbon and water, was given because most of them seem to indicate such a composition in their formulæ, $C_6H_{12}O_6$, $C_6H_{10}O_5$, $C_{12}H_{22}O_{11}$. This composition, however, is only apparent. They form such an important portion of the building material of plants and of the food of animals that a careful study of them is profitable. Externally they differ markedly (compare sugar and cellulose), particularly in regard to solubility and crystalline appearance. But all are made up of practically the same units, put together differently. We appreciate this in their classification. The first group includes the monosaccharides, for-

mula $C_6H_{12}O_6$: the name means that they are composed of single groups containing six carbon atoms. The second group of the classification is that of the disaccharides, formula, $C_{12}H_{22}O_{11}$, written better for our purpose $(C_6H_{11}O_5) — O — (C_6H_{11}O_5)$; this formula shows that they are made up of two of the monosaccharide units connected by means of oxygen. Their structure is similar to that of the ethers. It will be noticed that the difference between a disaccharide molecule and two monosaccharide molecules is water. The disaccharide is formed by the splitting off of water, H_2O, and the monosaccharide reformed by the addition of water to the double compound thus obtained. The third group is made up of the polysaccharides, formula $(C_6H_{10}O_5)n$. This formula is inadequate as the value of n is not known, but it conveniently indicates that the members of this group are made up of individual monosaccharides linked together as they are in the second class. The addition of water under the proper influences changes a polysaccharide into its constituent monosaccharides. In nature both types of changes, from the simple to the complex, and the reverse, are common. Artificially we can ordinarily accomplish only the simplification.

Inasmuch as the monosaccharide is the basis of all carbohydrates, we shall find that the study of this group will give us the chief information about the whole chapter. The most important monosaccharides are derived from hexane, the hydrocarbon of the paraffin series containing six carbon atoms. For five of these carbons one hydrogen is replaced by hydroxyl, and in the case of the sixth carbon, two hydrogens are replaced by a single oxygen. Two such combinations are found among the simple

SEALING THE DOORS OF THE COKE OVENS BEFORE TURNING ON THE HEAT

COKE COMING FROM THE OVENS AND DROPPING INTO THE CAR BELOW

sugars. $CH_2.OH.CHOH.CHOH.CHOH.CHOH.CHO$, is the formula for some of them, including the well-known dextrose or glucose. $CH_2OH.CHOH.CHOH.CHOH.CO.CH_2OH$ is the formula for others, including fruit sugar. These formulæ indicate the properties of the sugars. They must be solids, soluble in water, and sweet, to judge from their similarity to other compounds containing a number of hydroxyl groups. The sixth carbon, attached to the oxygen, represents an aldehyde or a ketone* structure, which gives the molecule the reactivity needed for a substance taking part in the vital processes. This reactivity is lessened by the building up of the double and complex carbohydrates, but as they are so readily reconverted into the simple molecules, the reactivity is in the end readily available.

There are three monosaccharides which are more important than the others. Glucose, also called dextrose or grape sugar, is the most common. It is widely distributed among plants, both as such, and as a constituent of di- and polysaccharides. It may therefore be made from starch and even from cellulose. The manufacture from starch is becoming increasingly important industrially. Glucose crystallizes with some difficulty, hence it is deliberately introduced or developed in candies to prevent their becoming "sugary." Glucose ferments readily, with yeast, while the more complex carbohydrates as cane sugar and starch do not ferment until they have been converted into the simple sugars. Glucose acts

* Ketones are similar to aldehydes. In the latter case the special group is attached to an end carbon, in the former case it is attached to an intermediate carbon. Aldehyde $CH_3.CH_2\ CO.H$, Ketone $CH_3\ CO\ CH_3$.

as food and plays a great rôle in the digestion and utilization of all the carbohydrates.

The second simple sugar is fructose, fruit sugar, levulose, one of the two constituents of the disaccharide, sucrose, or cane sugar. By itself it is of little moment, but as a product obtained by the splitting up of cane sugar it counts much. The third simple sugar, galactose, is, along with glucose, a constituent of the disaccharide, milk sugar.

In connection with the sugars, and other similarly complex compounds, there should be mentioned, even if not fully discussed, the fact that these substances exhibit what is called optical activity. If light of a certain kind (polarized) is passed through a solution of sugar, it is found to be affected. The plane of polarization is turned to the right or to the left. This is due to the arrangement, in space, of the various atoms around the nucleal carbon atoms. This has a very practical significance, in that it results in the formation of different sugars, glucose and galactose, which would otherwise seem to be identical. It serves also as a quick means, by help of the physical instrument called the polarimeter, of identifying and measuring sugars.

The Disaccharides. As was indicated above, the disaccharides are double compounds, made up of the union of two monosaccharides by the process of splitting off water. Acids, enzymes, and ferments readily break down ordinary cane sugar into its constituent groups, a process usually considered undesirable, yet possessing advantages in certain cases. Sucrose, saccharose, or cane sugar (this includes beet sugar, for there is no chemical difference) is the most highly esteemed of all the sugars. There are

several reasons for this fact. It occurs in several plants, cane, beet, maple, in such quantities that its extraction is easy. It is readily obtained in a pure and attractive form, and possesses the sweet taste in high degree. Its use is apparently on the increase. The sugar shortage of 1918, 1919, and 1920 illustrates very plainly how dependent we have become upon this form of food. In fermentation and digestive processes this disaccharide, like the others, is converted into monosaccharide before final changes take place. Its formula is usually written, $C_{12}H_{22}O_{11}$, but would be more suggestively written, $C_6H_{11}O_5 — O — C_6H_{11}O_5$, thus showing its double structure, like that of the ethers. The hydrolysis of this, like all other disaccharides, is expressed by the equation,

$$C_6H_{11}O_5 — O — C_6H_{11}O_5 + HOH \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6.$$

Milk sugar is of somewhat similar composition. It is crystalline, but not so soluble or sweet as cane sugar. It is so seldom separated from milk that we do not appreciate how much of it we consume. Milk contains five per cent milk sugar, that is, almost two ounces to the quart. This means a vast amount used as food throughout the country. The third common disaccharide is maltose, frequently formed as an intermediate product in the fermentation industries, but at once converted into alcohol. It is conceivable that, like glucose, it may find an application as a substitute for cane sugar.

The Polysaccharides. Dextrin, starch, and cellulose are the three polysaccharides of the greatest moment, and each of these probably occurs in several varieties. The formula for all polysaccharides is written $(C_6H_{10}O_5)n$, meaning that they are made

up of many glucose units, but the exact number of these units is unknown. It is likely that the value n is greater for starch than for dextrin, and still greater for cellulose. By treatment with enzymes and acids, these polysaccharides are caused to take on water, and to be converted into the constituent monosaccharide, usually glucose. Hence the great industry of making glucose from starch.

Dextrin is ordinarily found on the market as a transparent gum, somewhat soluble in water, possessing a slightly sweet taste, and giving a marked purple color with iodine. It is useful for such purposes as gumming postage stamps, and is an important intermediate product between starch and sugars.

The well-known polysaccharide, starch, is insoluble in cold water, but upon heating with water swells and becomes soluble. The insoluble granules of starch, as well as the solution, give with iodine a strong blue color, so pronounced that it serves as a delicate test for both iodine and starch. Starch from different sources may be distinguished by means of the microscope, but no chemical difference is apparent. Chemically considered, the most important feature of starch is its conversion by means of enzymes or acids into simpler compounds. With care at least five intermediate products may be distinguished, each one undoubtedly simpler than its predecessor, when starch is converted into its constituent monosaccharide, glucose. This change occurs in the digestive process, and also in manufacturing processes wherein glucose is made for its sweetening value.

There are a number of other polysaccharides. Inulin and glycogen are similar to starch, the latter

an intermediate compound in the process of the utilization of carbohydrate foods. The gums are similar to dextrin, but with this interesting deviation, that the constituent monosaccharide contains only five carbon atoms, being called a pentose, while glucose is a hexose.

Cellulose, best illustrated by the fiber of cotton, is more stable and less reactive than the previously mentioned polysaccharides, and therefore the inference is a fair one that it is more complex. Its value, of course, lies mostly in its use as a textile, but its chemical nature does count in some operations, as in making guncotton, collodion, and other products, as will be shown in the chapter on industrial organic chemistry. It reacts, upon proper treatment, as a regular polysaccharide, being broken down into its constituent glucose molecules.

NITROGEN DERIVATIVES

The importance of nitrogen in the composition of foods and the animal organism is now a matter of common knowledge. Unfortunately the chemistry of organic nitrogen compounds is a difficult subject and in a brief work like this must be touched on only lightly. It has already been pointed out that nitrogen derivatives are obtained by replacing hydrogen of a hydrocarbon by means of the residue $—NH_2$, obtained from ammonia. Three phases of this require attention in considering the most important compounds included in this chapter.

A. Derivatives obtained by replacing one or more hydrogens of a hydrocarbon by means of $—NH_2$. Example, CH_3NH_2, $C_2H_5NH_2$, $C_5H_{10}(NH_2)_2$. These have been sufficiently described.

B. An organic acid may have its acid group modified by the replacement of the hydroxyl group therein by means of —NH_2, thus forming an acid amide. Example, acid $CH_3.CO.OH$, acid amide $CH_3CO.NH_2$. The exchange is readily effected in either direction.

C. In the hydrocarbon part of an acid, the hydrogen may be replaced by —NH_2, forming the amino acids. Example, $CH_3CO.OH$, the acid, and $CH_2NH_2.CO.OH$, the amino acid. The chief interest of these lies in the fact that the all-important proteins are complexes made up of amino acid units.

Urea represents the excretory product of practically all of the nitrogen of the foods. The formula of urea is $CO.(NH_2)_2$, which, when compared with that of carbonic acid, $CO.(OH)_2$, shows that it is amide of that acid, in that the two hydroxyl groups of the acid are replaced by the amino group.

Related to urea we find a number of more complicated compounds, in which list are such substances as uric acid, $C_5H_4N_4O_3$, xanthine, $C_5H_4N_4O_2$, and caffeine, $C_8H_{10}N_4O_2$. They are a few examples of a long list of substances, many of them derived from the proteins, of the greatest interest in the study of biochemistry. Important as these substances are from that standpoint, they may only be mentioned here.

THE UNSATURATED PARAFFINS AND THEIR DERIVATIVES

A conspicuous feature of all the paraffin hydrocarbons and their derivatives so far discussed is that they are saturated, that is, all the affinities of the carbon nucleus are satisfied. No modification in these compounds can be made without first eliminating some atom or group of atoms already present. Methane, CH_4, can form a derivative only after the

loss of one or more hydrogens, the places of which hydrogens are then filled with the new group. The chlorine derivatives illustrate this, in that their formulæ are written CH_3Cl, CH_2Cl_2, $CHCl_3$. For each chlorine introduced a hydrogen must be eliminated. But by the proper manipulation of some of these compounds, we are enabled to remove hydrogen, always in pairs of atoms, without replacing it with compensating groups. Hence such substances must be unsaturated. C_2H_6 is saturated, C_2H_4 and C_2H_2 are unsaturated, and can evidently take on either hydrogen or some other atoms or groups to make up the equivalent of C_2H_6. We call this condition the unsaturated condition, and establish a new device of bonds or linkages to represent it.

Acetylene, C_2H_2, has a special interest. It is prepared easily, by an operation familiar to most, the action of water on calcium carbide. The high carbon content of the gas causes it to burn with a very luminous flame. These two facts have resulted in its extensive use for illuminating houses not connected with central lighting plants.

The unsaturated condition exists also in paraffin derivatives. Most important of all are the unsaturated acids occurring in certain fats, such as olive oil and linseed oil. The unsaturated condition of olive oil is the cause of its liquid condition, while linseed oil owes its peculiar value when applied to making paints to this fact.

Linseed oil is highly unsaturated, and tends to add other atoms to itself. To this fact it owes its drying property. Drying here does not mean evaporating, it means chemical changes of such a nature that the liquid substance becomes a solid. These chemical changes are due to the absorption of oxygen in place

of the lacking hydrogen, oxidation due to the triple bond, and perhaps also to polymerization, namely, union of the molecules with others of the same kind. The result is a solid, and linseed oil and a few other oils thus fill a unique place in the industries.

The use in foods of a solid or a liquid fat is to a considerable extent a matter of taste and usage. As the liquid fats, or oils, owe their liquid state to the unsaturated condition of the fatty acid, it is not unusual for such oils to decompose more readily, that is, become rancid, for the unsaturated condition means chemical reactivity. It is certainly true that, in cooking, solid fats are more popular than the liquid. Hence there has been developed the art of adding hydrogen to these liquid unsaturated compounds, converting them into solids and thus making an attractive compound out of an unattractive one. This process is called hydrogenation, and is used in particular to make the liquid cottonseed oil, which is unsaturated, and comparatively unattractive, into solid compounds, containing more hydrogen, of distinctly more inviting appearance and properties. Several of the much advertised shortening agents now on the market are of this description.

THE BENZENE OR AROMATIC SERIES OF HYDROCARBONS AND THEIR DERIVATIVES

Although all hydrocarbons are in many respects alike, the benzene hydrocarbons show some characteristics in which they differ from the paraffins. There is no such contrast as between metals and nonmetals, for example, but the differences are striking enough to make a differentiation possible and desirable. Four points of difference are to be observed. First, the benzenes contain less hydrogen than the

paraffins—compare benzene, C_6H_6, with hexane, a paraffin, C_6H_{14}. One might suppose that the benzenes would, therefore, act as unsaturated substances, tending to unite eagerly with more hydrogen or its equivalent. This is, however, only exceptionally true, and the benzenes act on the whole as saturated compounds. The derivatives are formed, as in the case of the paraffins, by the replacement of one or more of the hydrogens by other groups.

Secondly, the configuration of the molecules is peculiar. The carbons of the paraffins are held together in open chains, thus, C—C—C—C—C—C. In benzene the carbons are held together by the so-called ring structure, really a hexagon, The essential feature of this is that the units of the ring are all equally related to the whole. It would lead too far to explain the reasons for this assumption and the interesting features which it accounts for. As a matter of fact the assumption has been of the greatest value in the progress of organic chemistry. So typical is this ring of chemical thought that it was used in its conventional form as part of the device representing the chemical warfare service in the World War.

The third feature of the benzene hydrocarbons is that they have a noticeably greater reactivity than the paraffin hydrocarbons. They react especially readily with nitric and sulphuric acids. This has a very important practical outcome. In only very rare cases do the hydrocarbons of the paraffins serve as raw material for the making of the derivatives.

Their lack of reactivity is too great an impediment. By contrast, the benzene hydrocarbons lend themselves very readily to the preparation of all kinds of derivatives, for which the hydrocarbon is almost exclusively the starting point, or raw material.

In apparent contradiction to this characteristic of activity is the stability of the benzene ring. When this ring is a part of a more complex combination, it is often possible to completely destroy all the added parts, but the ring remains intact. For this reason a benzene derivative would not be suitable for foods, for foods must ultimately be completely oxidized. A benzene compound would go through the processes of metabolism in the animal body without being sufficiently disintegrated. We may summarize: Paraffin hydrocarbons are little reactive, but the carbon nucleus is rather easily disintegrated. Benzenes are reactive in that they readily form derivatives, but the carbon nucleus is a very stable one, persisting through a great variety of reactions.

The properties of the paraffins and benzenes just outlined naturally enough result in a very marked difference in their application. Taken all in all, the paraffin derivatives supply the material of living organisms, which includes, as has been seen, the most important substances used as foods, while from the benzene series is taken the mass of synthetic derivatives illustrated particularly by the dyes. The cause is, of course, in the greater reactivity of the benzenes. The ring lends itself to endless reactions, always preserving its own individuality as the nucleus of the whole.

Benzene, or benzol, must not be confused with benzine, a trade name for a mixed petroleum product

akin to gasoline. Benzene is a definite compound in the form of a colorless liquid solidifying at 6° C., and boiling at 80° C. It is lighter than water, in which it is insoluble. It is an excellent solvent for such substances as the fats. Its odor is mildly pleasant, and promises to become familiar to users of motor cars, as benzene is now frequently introduced into gasoline. For this purpose it could never be used unmixed, as it solidifies a number of degrees above freezing. Although it burns with a sooty flame, on account of its high carbon content, it is said to be satisfactory in respect to any deposits of that substance.

Just as methane, the first of the paraffin series, is followed by the other members, formed by the progressive substitution of the methyl residue for hydrogen, CH_4;$CH_3.CH_3$;$CH_3CH_2CH_3$, etc., so also from benzene a series is built up in more or less the same manner. It is not so long a series, being limited for all practical purposes to about ten members, although many more are known. These ten "homologues" are:

Toluene, $C_6H_5.CH_3$, (Toluol)
Three Xylenes, $C_6H_4.(CH_3)_2$ (Xylols)
Three trimethyl benzenes, $C_6H_3.(CH_3)_3$
Ethyl benzene, $C_6H_5.C_2H_5$
Cumene, $C_6H_5.C_3H_7$
Cymene, $C_6H_4.CH_3.C_3H_7$

It will be noted that these formulæ always show a benzene nucleus to which the paraffin residues are attached. In a complete study of our subject, we would need to give great care to the fact that such hydrocarbons yield two sets of derivatives, those obtained from the original ring, and those obtained from the paraffin residue. The latter repeat the char-

acteristics of the compounds already outlined under that head. The former, however, yield compounds of the new type, those typical of the benzene ring. Two illustrations will suffice. $C_6H_5.CH_3$ yields $C_6H_5.CO_2H$, benzoic acid, wherein the variation is in the paraffin residue entirely, and the benzene nucleus is unchanged. While in tri-nitro-toluene, "T.N.T.," $C_6H_2(NO_2)_3CH_3$, the benzene nucleus is the one affected. Salicylic acid is typical of compounds in which both residues are affected, $C_6H_4OH.CO_2H$.

The application of these hydrocarbons as such in the industries is somewhat limited. They are useful as solvents, and the more volatile will in all probability be used to supplement the paraffin products for motor fuel. Their great use is to prepare "intermediates," compounds which are later developed into the finished coal-tar products.

DERIVATIVES OF THE BENZENES

(*a*) C_6H_5Cl, halogen compound (*d*) $C_6H_5NH_2$, amino compound
(*b*) $C_6H_5SO_3H$, sulphonic acid. (*e*) C_6H_5OH, phenol
(*c*) $C_6H_5NO_2$, nitro compound

The above table shows the simpler derivatives obtained from benzene itself, and they are types also of compounds obtained from the benzene nucleus of any other members of the series. Those of the first column are obtained directly from the hydrocarbons, while those of the second column must be prepared indirectly by first forming a compound of the first group.

A. The halogen derivatives are of minor importance, although in some of the more complex forms they are useful. They are obtained with great ease by the direct treatment of the hydrocarbon with chlorine or bromine.

B. The sulphonic acids are valuable intermediates, being readily transformed into other desired compounds. This sulphonic acid group in itself introduces certain properties of value. Its presence results in solubility and reactivity which previously may have been lacking.

C. The products obtained by treating the benzene hydrocarbons with nitric acid are called nitro compounds. $C_6H_5NO_2$, $C_6H_4(NO_2)_2$ and $C_6H_2CH_3(NO_2)_3$, T.N.T., are examples. Like the sulphonic acids these compounds have a certain value of their own, as in dyes and explosives; but they also serve as intermediates for the formation of other compounds.

D. The amino compounds. Type, $C_6H_5NH_2$. This is the famous aniline, so valuable as an intermediate for the manufacture of many of the dyes. It has some properties of ammonia, NH_3, due to the amino group, $—NH_2$, but the benzene nucleus is very prominent. Aniline is a liquid, only slightly soluble in water, and poisonous when absorbed in any considerable amount. In ordinary use no harmful effects are noticed, but factory operatives do feel it and especial attention is required in avoiding its evil effect. Just as the amino group introduced into a benzene nucleus forms aniline, so the corresponding compound from toluene is toluidine, $C_6H_4NH_2CH_3$, with similar properties; and these are but typical of the many benzene amino compounds, over a hundred in number. They are formed according to the simple principles of substituting the amino group alone, or with others, in the benzene nucleus of these hydrocarbons.

E. The phenols. Type, C_6H_5OH. The phenols have a composition akin to that of the alcohols, and consequently many chemical characteristics in common. Yet the benzene nucleus introduces other char-

acteristics, the most striking of which are poisonous character, and acidic nature, in contrast to the paraffin alcohols, which are basic. This is shown in the names commonly applied, carbolic acid for ordinary phenol, and cresylic acid for cresol. The chief member of the group of the phenols is the well-known carbolic acid. It is an easily melting crystalline solid, which assumes the liquid state when small amounts of water are mixed with it. It is usually slightly colored with small amounts of impurities, and only slightly soluble in water. The pure substance has a pleasant odor. It has valuable antiseptic properties, and is well known to be poisonous. Other phenols are formed when the hydroxyl group is introduced in other benzene hydrocarbons, and they have the same valuable properties. Thymol, $C_6H_3.OH.CH_3.C_3H_7$, in particular finds application in medicine.

In accordance with the usual modifications of organic compounds, there exist phenols containing more than one hydroxyl group, $C_6H_4(OH)_2$, resorcinol, and $C_6H_3(OH)_3$, pyrogallol. These are soluble in water as the several hydroxyl groups have greater influence. These find application in photography and other chemical manipulations.

The presence of the hydroxyl group in phenol in no way interferes with the introduction of other groups. One of these is picric acid, $C_6H_2\begin{matrix}OH\\(NO_2)_3\end{matrix}$, useful as a dye and as an explosive.

DERIVATIVES INVOLVING THE PARAFFIN RESIDUE OF THE HOMOLOGUES OF BENZENES

In toluene, $C_6H_5CH_3$, we have two possibilities of derivatives, such as are obtained from the benzene

portion, C_6H_5, and such as are obtained from the paraffin portion, CH_3. The latter simply repeat in a manner the compounds of the paraffin chapter. The most important are $C_6H_5.CH_2OH$, C_6H_5CHO, $C_6H_5CO_2H$, respectively benzyl alcohol, benzaldehyde, and benzoic acid. The aldehyde, oil of bitter almonds, has a pleasant odor and flavor, and the aldehyde group attached to the benzene ring is often associated with these conditions. Vanilla, for example, contains this group. Benzoic acid, as well as its sodium salts, is used as a preservative. It is a mild acid, differing markedly in activity from the more familiar type of acids. Other compounds of these types are not uncommon. Salicylic acid, $C_6H_4.OH.CO_2H$, is a double compound, containing both the acid and the phenol groups. Like benzoic acid it is used as a preservative, and it is one of the constituents of oil of wintergreen.

We have thus run over briefly the list of benzene derivatives. The number is very great, but some impression of their chief features may have been obtained. We have not touched to any considerable extent on the subject of mixed derivatives, compounds which like salicylic acid contain more than one substituting group. Their number is legion.

There is an interesting set of compounds, similar to benzene compounds, which are based upon nuclei somewhat differently constituted. Each of these nuclei is the basis of its own set of derivatives. It is interesting to call attention to them, but most of them repeat the properties of the benzene compounds. Such new nuclei give rise to the chapter on the terpene, diphenyl, naphthalene, anthracene, triphenyl methane, and pyridine derivatives. They will be taken up in the briefest possible fashion.

The terpenes, $C_{10}H_{16}$, contain both benzene and paraffin residue, and the former is modified by variations in the linkage, which give the terpenes an activity resembling that of the unsaturated paraffin hydrocarbons. This chapter includes about a hundred hydrocarbons, and many oxygen derivatives. In the list are turpentine, camphor, lemon oil, menthol, and many other of the well-known essential oils. Rubber, too, is included, so that this chapter presents a formidable list of compounds which are of frequent application.

Diphenyl, $C_{12}H_{10}$. The formula for diphenyl shows that two benzene rings are held together for the new nucleus. Naphthalene, $C_{10}H_8$, known in moth balls, has two benzene rings likewise, but they have two carbons in common, while anthracene, $C_{14}H_{10}$, has a similar structure involving three rings.

Triphenyl methane, $HC(C_6H_5)_3$, has three independent rings held together by one carbon. The chief interest attached to all these is that they are the nuclei of many valuable dyes, for the dyes depend upon an accumulation of carbon, which these substances supply in a striking way. In general the benzene rings which are present show all the characteristics of the ordinary benzene ring, and their derivatives are of the types already discussed.

Pyridine is the best known example of a ring made up in part of another element besides carbon. Of the six units required for the ring only five are carbon and the sixth is nitrogen. This gives the ring some new properties. This ring and others similar to it, form the nuclei for the well-known class of drugs and poisons known as the alkaloids. They include morphine, nicotine, quinine, cocaine, strychnine, and other substances of this type.

CHAPTER XXIII

THE ORGANIC CHEMICAL INDUSTRIES

THE practical side of organic chemistry touches our lives at many points, as is most natural, for our living processes and materials are parts of organic chemistry. The most important phases of the subject, biochemistry and foods, will be relegated to a considerable extent to the chapter on nutrition and agricultural chemistry. Other chapters, like that on petroleum, were conveniently discussed in the regular organic text. Still other chapters are conspicuous and will receive attention here.

There is no important basis for ordering these chapters and they will be discussed in the order suggested by the nature of their interest. However, it may be stated that the ordinary products of nature and their modifications involve compounds belonging to the paraffin series, while substances of a more artificial type, like the coal tar dyes and some of the explosives, belong to the benzene series.

THE CARBOHYDRATE INDUSTRIES

Glucose, maltose, sucrose, dextrin, starch, and cellulose are the carbohydrates which figure largely in the industrial world. Cellulose falls under the textiles. All of the rest, excepting sucrose, are alteration products of starch, so that in the discussion of sucrose and starch we will cover most of the field.

Cane sugar, saccharose or sucrose, is obtained mostly from the sugar cane and the sugar beet, and, in spite of the popular impression, there is no difference in the fully refined products. The extraction from the two sources is by different methods: from the cane by pressing out the sap, from the beet by diffusion into water. In each case the sugar solution obtained is then evaporated to obtain the solid sugar. In the case of the beets, the beets are chipped and then systematically extracted by means of separate lots of water. We here have an illustration of a device much employed in chemical engineering. The fresh chips, holding much sugar come in contact with the extracting solution when it is almost at the end of its absorbing capacity, while the beets which are almost exhausted are treated with the fresh water, and so on through, so that there is a maximum of extraction with a minimum application of water.

After the aqueous solution is separated from the fiber, the sugar recovery is essentially the separation of what gummy, resinous, and albuminous matter can be removed by a coagulant, the evaporation to the point of crystallization of the sugar, and finally the refining of the crude product. There are many steps and details, too technical and involved for mention here. A considerable amount of foreign matter accumulated toward the end interferes with further crystallization. Therefore there is a mother liquor, high in sugar content, which is the molasses. In the case of cane sugar this molasses has attractive properties and is to some extent utilized directly, but part of it is treated further for its sugar content.

The maple tree is in certain regions a source of sugar. Maple sugar owes its attractiveness to the delicate flavor of the foreign matter present, and no

doubt to its romantic source. It is ordinarily an article of luxury, used as a sirup, and commands a price, in accordance with its sugar content, of from two to three times that of ordinary sugar. Sorghum "molasses" is too impure for profitable extraction, but is used in localities as a sweetener for home consumption.

Starch is manufactured in large amounts, being extracted from corn, wheat, potatoes, and rice. Arrow-root starch, a very pure form, has some uses, while certain palm trees yield sago. Tapioca comes from a tropical plant. The last two are artificial modifications of the original product, hence their special form and appearance. The process of starch extraction is in great part mechanical, but fermentation processes are used to assist in the liberation of the starch grains from the other material present. Starch is used as food and in laundry work; in the textile industry it is used for dressing goods, as a thickener, and for sizing paper; it is used for paste and for making dextrin and glucose. The maltose formed in some industries, as in brewing, is usually made from starch still incorporated in the grain, and is not separated out as a pure product. During the time of sugar shortage there were rumors of the production and use of maltose as a sugar substitute, and such a development is easily possible.

Solid dextrin is made by the action of heat, or of heat and acids, on starch. It is used for its adhesive value (British gum). When diastase is used the product is sirupy, and is applied as such in candy making and in brewing.

In the making of glucose from starch the process of hydrolysis, that is, the splitting of the highly complex starch into simpler complexes, and finally

into its constituent units, is practically complete. In dextrin the molecule is a less complex polysaccharide than that in starch, in maltose we have a disaccharide, while in glucose we have reached the monosaccharide stage. The starch is heated with water and one to three per cent acid for an hour or more. The acid is then removed by means of calcium carbonate (marble dust) and the by-product, calcium sulphate, allowed to settle out. Glucose is usually applied as the thick sirup, but the dry sugar is also available. The popular prejudice against its use has almost died out.

THE OILS, FATS, AND WAXES

Although the liquid oils have a larger percentage of unsaturated fatty acids than do the solid fats, the distinction between them is on the whole a practical one, in that the name oil is applied to fats which are liquid at ordinary temperatures. The word oil is carelessly used to denote a number of unrelated substances, being applied to such different substances as petroleum, oil of wintergreen, and even sulphuric acid, and to obviate any confusion the substances discussed in this chapter could be designated as the fatty oils, or better, the liquid fats. Solid and liquid fats are use interchangeably to some extent, and if need should arise could be interchanged even more. Tradition and usage are firmly fixed, and long-established habits are altered only slowly. Another distinction which is from a chemical standpoint arbitrary, is that of animal and vegetable origin. Prejudice here too plays a part not justified by any difference in chemical composition. But attractiveness and minor convenience play a rôle which must be reckoned with in any practical consideration.

Fats are esters or salts, in which the base is invariably glycerine. This triple base requires three molecules of acid to combine with it, and these molecules may be the same or different. The acids are the higher acids of the fatty acid series, saturated and unsaturated, and it is seldom that only one acid is present in a fat. However, a fat from any given source is usually of the same approximate composition.

As the different constituent acids do not vary much in their properties, so the fats formed from them are very similar. But such differences as there are in the acids appear in their salts, the fats, and it is by these differences that the fats are chiefly distinguished and their uses to some extent determined. The chief differences are two. (*a*) The position in the fatty acid series. This determines whether the molecule is a comparatively small or large one. Yet the range is not great except for butter fat, which is conspicuous for containing about six per cent of the very low fatty acids, and butter fat is readily recognized by separating out and testing these acids. (*b*) The saturated or unsaturated condition of the acid counts for even more. When the unsaturation is slight, the practical result is a liquid condition of the fat. When more marked, we have the drying oils with unique properties and special uses in making paints and varnishes.

The composition of the waxes is distinct. Waxes also are salts or esters, but the base, instead of being the triple base glycerine, is a monoacid alcohol, one of the higher alcohols of the series. Beeswax is typical, melissyl palmitate, $C_{30}H_{61}(C_{16}H_{31}O_2)$.

The waxes are more stable than the fats, are less abundant, and of course have less application. They

are used chiefly for candles, for pharmaceutical preparations, and have various mechanical applications.

The presence of fats in vegetable as well as in animal organisms is a familiar fact. Nuts are conspicuous for their oil, and we are very familiar with olive, cottonseed, and linseed oil. In animal rations fats and carbohydrates supplement each other, serving more or less the same purpose, but practically no carbohydrate is stored by the animal. In the storing by vegetables, carbohydrates are more abundant than fats, and only when the former drops off is the latter abundant, as is illustrated in nuts. The animal fats in greatest use are lard, tallow, and butter fat. The vegetable fats best known are those from seeds, castor, cottonseed, hempseed, linseed, poppy, and sunflower; from nuts, walnut, almond, peanut, cocoanut; also olive oil, palm oil, and cocoa butter.

Fats are in the main extracted readily enough from the fiber and other material in which they are imbedded. They are easily melted, when not already liquid, and are thus extracted, especially with pressure. Or they may be extracted by means of solvents like gasoline and carbon disulphide, which dissolve out the fats without affecting other ingredients. The first use of fats is for foods; not alone for such uses as those of butter, olive oil, and lard, but a large amount is taken more or less unconsciously in the food, as in milk, oatmeal, and prepared dishes. Soap making may be considered next in interest. Its preparation has been discussed under the head of sodium in a previous chapter. Much fat is hydrolyzed, instead of being saponified, and this operation liberates the free fatty acids for any use desired. The free fatty acids can then be used for making soap, by uniting with sodium hydroxide (lye) or

they can be used for making candles, as they are solid enough to be firm, yet melt easily as the candle is burned, and are readily vaporized at the wick. The paraffin used so much for candles is mechanically imperfect, as it softens too readily in warm weather. Tallow and the natural waxes are also used for candle making. The fatty acids are advantageously mixed with paraffin for the better grade of candles, as they make them firmer and therefore less likely to collapse or to drip.

Fats and fatty oils are used as lubricants, in medicinal preparations, as ointments, and in various textile operations, as treatment of hides in making leather. The unsaturated oils have a unique application in paints and varnishes.

The hardening, or hydrogenation, of oils is a most interesting process which has come into prominence in recent years. The liquid fats are usually not considered as serviceable as are the solid. This may be due to the mere liquid condition or to the fact that some of them are less stable, and readily become rancid. The chemical feature of these liquid fats is that they contain less hydrogen than solid fats. As an example, the fat, $C_3H_5(C_{18}H_{35}O_2)_3$, is a solid. The corresponding liquid fat is $C_3H_5(C_{18}H_{33}O_2)_3$. Upon treatment with hydrogen in presence of a catalyzer (nickel is much used) enough hydrogen can be added to the liquid fats to convert them into solids. Cottonseed oil is thus made into a very attractive solid product.

Glycerine belongs to the chapter on fats. The formula shows that the proportions of glycerine obtained from a fat must of necessity be small. Stearin yields only 10 per cent of its weight theoretically. Its chief use is for nitroglycerine, one of

the great agents of modern engineering. Other applications are in toilet soaps, pharmacy and medicine, antifreeze, and for keeping fiber moist and soft, as it does not evaporate and attracts small amounts of water from the air.

THE FERMENTATION INDUSTRIES

The process of fermentation is usually associated with the formation of ethyl alcohol from sugar or starch. Yet other alcohols are obtained at the same time and are valuable by-products. Such a one is amyl alcohol, named on account of its relation to starch. Vinegar making is a fermentation process and other acids as butyric and lactic are also formed by similar methods.

The simplest form of alcoholic fermentation is that of glucose, or mixtures of glucose and levulose, the sugars of ordinary fruit juices. Almost as soon as this juice is extracted, that is, exposed to the air, spores fall into it and fermentation begins.

Alcoholic fermentation requires no chemical reagent from without, the change being simply the rearrangement of the hydrogen and oxygen already present. Ethyl alcohol and carbon dioxide are such predominating products that other substances formed are little considered. Besides alcohol and the residual sugar, the acids from the fruit are important, not alone for their own acid taste, but also on account of their delicately flavored esters or organic salts which they develop with the alcohols. These, as well as other foreign substances are present in small amounts, but these small amounts are sufficient to influence the taste of the product. One familiar with the wine industry knows the great importance of delicate gradations in flavor when no

other difference can be established. The details of wine making are many, and the industry is taken very seriously in wine-growing regions, like that of the Rhine, where schools for its study are established. Cider making is familiar, yet it is an illustration of a common experience with very little knowledge of the nature of the real facts. In this process the course of the changes is as follows: The sugar begins to ferment very promptly, and in two weeks the sugar may be mainly converted into alcohol. The cider now seems sour, not on account of the increase in acid, but on account of the decrease in sugar, so that the sour taste of malic acid originally present in the apple is apparent. If not protected from the air (oxygen and mother of vinegar) acetic acid fermentation may now begin. Ten per cent of sugar should yield theoretically a five per cent alcohol solution, and a vinegar containing 6.7 per cent acid. The usual result is a lower one, and ordinary vinegar contains about four per cent.

The essential feature of the brewing industry is that the sugar to be fermented is obtained from the starch of grains. Malt is barley partially germinated, there being formed the enzyme diastase, which is capable of converting starch into maltose. It is this maltose which ferments under the influence of yeast. From the standpoint of the brewing industry these statements are most meager. There are many fine points involving economy, flavor, and keeping which would involve a highly technical discussion.

The third class of alcohol industries involves the concentration by distillation of the alcohol formed in one of the above fermentation processes. When the raw material is the fermented fruit juice, brandy

is the product. Sugar residues yield rum, and the various grains, fermented, yield whiskey. The alcohol content of these beverages is roughly 40-50 per cent, and the difference lies mainly in the small amounts of other ingredients, such as flavors, color, and other alcohols besides ethyl. These last are supposed to be injurious. These details are given weight in popular interest out of all proportion to their importance in the eyes of a chemist. On the other hand, the chemist should not put too light an estimate upon popular impressions concerning minute differences in much used articles. They may contain the germs of important truths.

The manufacture of alcohol as such is a phase of the distillation process. Grain is allowed to ferment, alcohol is developed and then distilled off. Stills have been designed which accomplish a satisfactory separation of the alcohol and water in one operation, usually no easy affair. The apparatus is so arranged that the vapors do not at once go to the condensers, but are retarded with the effect that the more easily condensible water is in part returned to the still, while the more volatile alcohol retains the vapor form and so passes on to the main condensers. From such a still alcohol of high percentage may be obtained. For absolute alcohol, that is, 99 per cent or better, the water must be removed by chemical means. In order to avoid the hindrance to the industries due to the tax on beverages, and now due to prohibition of this industry, denaturing is resorted to, in order to make the alcohol available for the one purpose and to prevent its use for the other. Wood alcohol, mixed with pyridine, is much used as a denaturant, and though not ideal, has served the purpose reasonably well.

PERFUMES, FLAVORS, AND THE ESSENTIAL OILS

Although the substances collected from the ends of the earth for the satisfaction of men's desires along these lines are gathered with no reference to their chemical nature, they have some chemical resemblance, and when their chemical structure is understood it is seen that they fall into one of a very few classes. They are vegetable products; sometimes so nearly a pure simple compound that the artificial duplication is practically identical, sometimes so blended with small amounts of various other constituents that their properties can only be crudely imitated. The name essential oils applied to many of them must not be misunderstood. They are not oils, and simply possess some of the external characteristics of oils. For purposes of food (flavors), personal enjoyment (perfumes), and medicinal value these comparatively rare substances play an important part. The industry is to some extent a haphazard one, the products being gathered up here and there as stray producers or collectors provide them. But taken all in all, especially for a few favorites, such as camphor, vanilla, and peppermint, the amount produced in the end is large, and they are important articles of commerce.

The classification of these substances is as follows:

1. Compounds containing oxygen. These are both paraffin and benzene derivatives containing one or more of the groups; esters, ethers, alcohols, aldehydes, phenols, or ketones. Banana oil is amyl acetate. Vanilla, $C_6H_3(OH).(CHO)\ (OCH_3)$, includes three of these groups.

2. The second class is included in the group of the terpenes, $C_{10}H_{16}$. This group includes not only the

hydrocarbons, but certain oxygen derivatives. The hydrocarbons themselves possess unique properties, and form a group of over a hundred individuals. Clove and lemon oils belong here, as also caraway, rose, orange, peppermint, camphor, and many others.

THE COAL TAR INDUSTRY

The forms of soft coal which are distilled for the making of coke are popularly looked upon as forms of carbon, with considerable impurity. When we consider it from the present standpoint, we must appreciate that soft coal is probably a compound of carbon, very rich in carbon, to be sure, but still a compound. Formulæ like $C_{24}H_{18}O_3$ have been suggested, although there are also small amounts of nitrogen compounds present. When this coal is heated, the highly complex molecule decomposes before it can volatilize, and the atoms present rearrange themselves in more simple and stable forms. These are the products of coal distillation. The purpose of the distillation of coal is in the coal regions to produce coke, in the cities to produce gas, but the operation is in each case the same. The soft coal is placed in retorts which are heated from without, and the gas begins to pass off at once. The gas consists mostly of hydrogen and methane, over 80 per cent, and when it is to be used for illuminating purposes without a mantle, needs to be enriched by the addition of other hydrocarbons high in carbon. But there is a growing tendency to use the gas for heating purposes, therefore to neglect the enriching, and if light is needed, to make use of the Welsbach mantle. Besides the gas, which needs some purification, there is obtained by condensation an aqueous liquid containing ammonia. This is not

only the source of all the ammonia used as such for ice machines and other purposes, but much of it is applied simply as a convenient nitrogen compound in fertilizers. Ammonia may be oxidized to nitric acid, to be used for explosives. This last application is likely to be limited to the exigencies of war time.

The most interesting product from our standpoint is the tar. About 20 per cent of the weight of the coal appears in this black confused mixture of all the nonaqueous liquids formed in the process. This is distilled to obtain the various products, but about half of it remains behind as a pitch, of such a nature that it must be used simply as a tar for roofing, paving, and similar crude purposes. About 40 per cent of the coal tar can be separated into various hydrocarbons: benzene, toluene, xylene, cumene, naphthalene, and anthracene, which are used in part for the raw material of the benzene products, and in part as solvents and fuel. Of another type are the products of the phenol group, so-called carbolic and cresylic acids, valuable as antiseptics and disinfectants. Pyridine and a number of minor products are obtained in addition.

Though these products are to some extent applied directly in a more or less purified form, their chief interest lies in the fact that they form the raw material for the manufacture of the intermediate and finished products of the much-talked-of drugs and dyes. Specific as it is, the subject is one of far-reaching interest, for the deprivations of the war showed that the dye industry is a key industry, that upon it depend so many other industries that its stoppage was felt in many lines. It is the opinion of most American chemists that this branch of

chemistry in both its theoretical and industrial aspects should be fostered with the greatest care.

The dyestuffs will be discussed under the topic of textiles. The industry is an elaborate one and requires the application of many complex processes. From the coal tar, mentioned above, nine crude products are obtained, mostly hydrocarbons. These are made into almost 300 secondary products, called intermediates, and from these about twelve hundred finished products are prepared, three-quarters of them dyestuffs. However, only about half the dyestuffs are actually manufactured and used, as these seem to be sufficient to fill the needs.

THE TEXTILES—CELLULOSE, WOOL, SILK, RUBBER, LEATHER

In the use of these materials the physical properties are the outstanding features which regulate their value. But the chemical composition is interesting in itself, and the knowledge thereof leads to modifications which are of great value.

The chemistry of cellulose has already been explained under the heading of carbohydrates. Cellulose represents the composition of cotton and linen. The other cellulose fibers, hemp, jute, ramie, contain the cellulose either in modified form or in combination with a modified woody form. Their properties are determined by such characteristics as the length of the fiber, its pliability, its heat conductivity, strength, and brittleness.

On the whole cellulose is an inactive insoluble substance. Yet its chemical properties are made available in a number of instances.

A. With nitric acid, concentrated by the addition of sulphuric acid, cellulose forms a number of differ-

ent nitrates, depending upon the completeness of the action. Using a formula containing two monosaccharide groups, twelve carbon atoms, for cellulose, there may be said to be introduced six or less nitrate groups, in that the cellulose acts as a base. The first of these is guncotton, and from the others valuable products are made. By the solution of these nitrates in alcohol and ether mixture, or other solvents, collodion and other articles of that general nature are made. Incorporation with camphor forms celluloid. The well known combustibility of photographic films is due to the nitrocellulose of which they are composed. Nitrocellulose is also used in making vegetable silk.

B. Hydrochloric acid disintegrates cellulose very readily, and cotton is frequently removed from wool by treatment with this reagent.

C. Sulphuric acid acting slightly seems to accomplish a partial hydrolysis. To this action may be attributed the formation of amyloid, which turns blue with iodine, and of the gummy material which makes parchment paper so strong. Further action of sulphuric acid in presence of water converts cellulose into the monosaccharide, glucose.

D. Sodium hydroxide solution applied to cotton fiber mercerizes it. That is, the fiber swells, shortens, becomes stronger and has a silky effect.

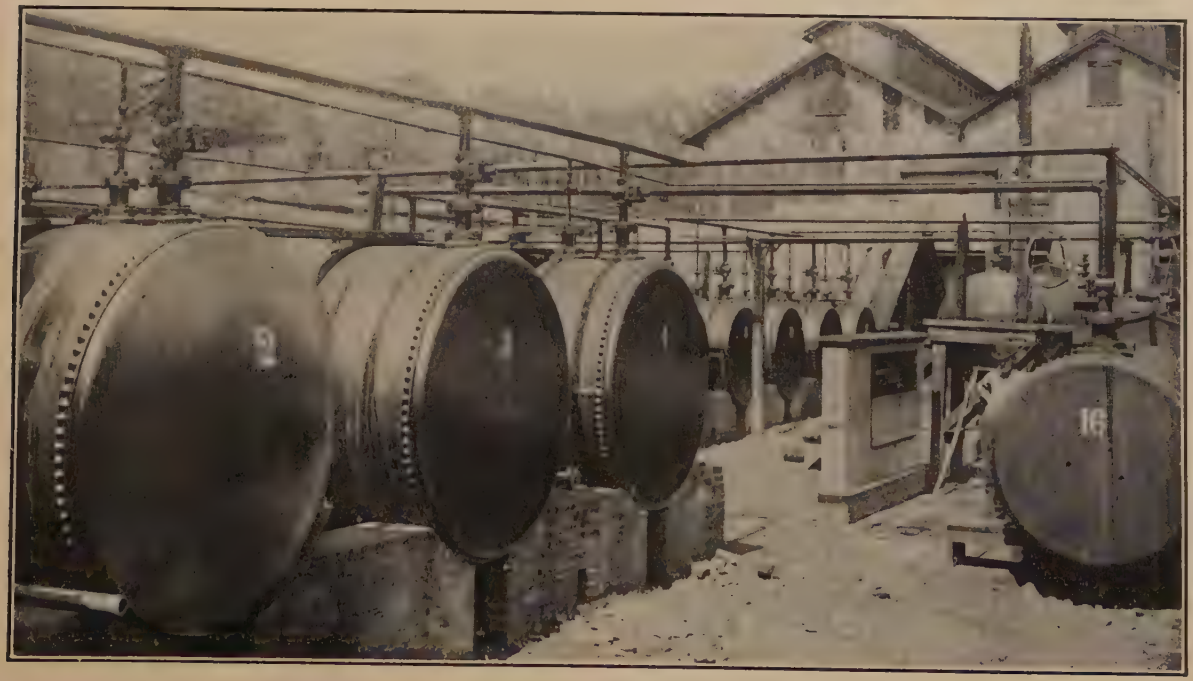
E. Vegetable silk. The process of making vegetable silk is the conversion of cellulose into a jelly, which can then be squeezed out into a thread and hardened as is the jelly of the silk worm. Solution of the cotton, chemically modified, if necessary, in a solvent with which it forms a jelly is the first step. Squeezing this jelly out through fine openings to form a slender thread is the second step. Setting

the thread is the third. Nitrocellulose, dissolved in alcohol and ether, and later denitrated by means of ammonium sulphide is one method of obtaining such a jelly. A solution of cellulose in Schweitzer's reagent, copper sulphate and ammonia, represents another process. The thread is set by treatment with acid. Still another method is the solution of the cellulose in a mixture of sodium hydroxide and carbon disulphide. The thread is set by means of ammonium sulphide.

Wool is a protein in its chemical structure. This means that it is very complex, that it contains nitrogen (it also contains sulphur) and is made up of amino acids held together by an ammonia residue. Wool is therefore amphoteric, that is, it has both basic and acid nature, a matter of great moment in the application of the dyes. It does not burn readily, and when it does, gives off the "burnt feather" odor. Toward bleaching agents wool is rather sensitive, and may not be treated with chlorine. Sulphur dioxide and hydrogen peroxide are satisfactory bleachers.

Silk is also a protein, without sulphur. The setting of the gelatinous thread spun by the worm into the silk fiber is similar to other coagulations (white of egg) of proteins. Silk, like wool, is amphoteric.

These textiles are often loaded with foreign substances for the purpose of accomplishing certain results. They are impregnated with salts to render them less inflammable, an important matter with lighter fabrics. They are impregnated with gummy materials, as starch, for stiffness, with fats and soaps to make them soft, and with various compounds to give them body and weight. Some silks are made up of more than half added material.



SULPHURIC ACID TANKS AT A SMOKELESS POWDER PLANT

GUNCOTTON ON THE WAY TO THE MIXER WHERE MANUFACTURE OF SMOKELESS POWDER IS COMPLETED

Leather differs so much externally from the fibers just discussed that it is not usually classed with the textiles, yet the chemical composition of leather is much the same as that of wool. The essential portion of the hide is the dermis or true skin. When this ordinarily dries, a substance like glue or gelatin, the coriin, in among the fibers, stiffens, and this cements the whole together into the hard mass familiar in dried skins. The tanning operation seems to be the combination of the tanning materials with this coriin, thus altering it, so that it is no longer capable of this cementing action. It is interesting that the tanning materials are the same as those used for mordants in dyeing. Tannin, a compound of doubtful composition, derived from gallic acid, the best known of the tanning materials, is obtained from various sources, such as oak and hemlock bark. Metallic compounds are also used, especially those of chromium and aluminium. In the latter case the compound formed is unstable, being decomposed by water, hence such leather is spoiled by wetting. In the case of oil tanning the process is aided by a removal of as much of the coriin as possible.

Rubber or caoutchouc has the formula $C_{10}H_{16}$, and therefore belongs to the terpenes. It is very inactive and insoluble, yet a number of laboratory reagents attack it readily. A number of years ago artificial rubber, made from isoprene, C_5H_8, received much attention and seemed of great promise. But in cost it could not compete with the rubber produced in the ever-increasing rubber plantations, and lately artificial rubber is little heard of. The most important chemical feature of rubber is the formation of a compound with sulphur. Unaltered rubber softens upon warming, and can thus be shaped, but when it

is heated after being mixed with sulphur or sulphur compounds this property is altered and the rubber becomes more permanent. For the making of rubber articles, the rubber is mixed with considerable amounts of inert materials, as resins and chalk.

DYES AND DYEING

A scrutiny of the compounds of organic chemistry will reveal the fact that they are chiefly colorless. The few colors which are noted in the preparation of organic substances are either due to the inorganic elements, as iodoform, or to impurities, probably of a complex nature. Color is associated with a very special structure of a somewhat elaborate molecule. The conditions which must be fulfilled are, first, that there must be an accumulation of carbon in the molecule. It will be apparent that the dyes must then be derived from the benzene series, C_6H_6, rather than from the paraffin series, C_6H_{14}, for in the latter the carbon is diluted, so to speak, with twice as much hydrogen as in the benzene compounds. A second condition for color is that there shall be present a special combination of atoms, in a group called the chromophor (color-bearing) group, and to this group the color is due. In some cases this group is pretty well defined, in others less so. The possession of color alone is, however, not enough to constitute a dye. The substance must also possess such chemical characteristics that it will form a compound with the fiber which is to be dyed. The commonest relation of chemistry is that of the acids and bases, and we find that repeated here. The dyestuffs must contain an acid group, SO_3H, OH, or CO_2H, or a basic group, NH_2. Without one of these they will not attach themselves directly to fiber.

Wool and silk being amphoteric, react readily with all dyes, as acids to basic dyes, and as bases to acid dyes. Cotton, however, not having such pronounced chemical properties, does not ordinarily respond and requires a mordant or go-between. However, there are some conditions under which it is advisable to use a mordant with wool and silk, and there are some dyes of such chemical activity that even cotton will unite directly with them.

These combinations are very definite, and an alteration in the chromophor group may destroy the color of the dye. Indigo is easily converted into a compound, indigo white, which, because it lacks the chromophor group, is colorless. Changes in the rest of the molecule in the way of increasing its complexity often enhance the color value of the dye. The simplest dyes are yellow, but if the structure is made more complex, the color intensifies, yellow to orange, then red, purple, and finally blue or green.

The process of dyeing is probably more than the simple impregnation of the fiber with the color. It is perhaps a chemical union of the dye with the fiber, resembling in many respects the simple union of base and acid. The fiber is placed in a dilute solution of the dye, containing dye to the extent of 1 to 3 per cent of the weight of the fiber, and the whole is heated with careful mixing for about thirty minutes. The fiber will now have taken all of the dye with which it can unite, and the process is practically done. When cotton is to be dyed a mordant must often be used to bind the dye to the fiber. For basic dies, the mordant is acid, as tannin and the fatty acids of oils and soaps. For an acid dye the basic mordants used are the oxides of aluminium, iron, chromium, tin, antimony, zinc, and lead. Some

of these influence the color, and advantage is taken of that fact.

THE ORGANIC EXPLOSIVES

Explosives owe their efficiency to the rapid development of gases, which, owing to their great bulk, must find some vent. Inasmuch as these explosions are accompanied by a heat development, there is added force given to the gases by the expansion due to the heat. Finally the suddenness of the action is the most important factor in the shattering effect of the explosive. In the old black powder the carbon and sulphur present burn at the expense of the oxygen of the potassium nitrate, and three gases, carbon dioxide, carbon monoxide, and nitrogen, are formed. These gases form comparatively slowly, so that the shattering effect is slight. In a high explosive, on the other hand, like nitroglycerine, $C_3H_5(NO_3)_3$, all the atoms entering into the action are exceedingly close to each other, being parts of the same molecule. It is estimated that its disintegration is about a thousand times as rapid as is that of black powder, hence its violent shattering effect.

Explosives are of two main types, the high explosives, used purely for shattering, as for blasting and for filling shells in warfare. Decomposition is so rapid, and the force of the shock applied so suddenly, that its force cannot be transmitted to the movement of any body as a whole. Hence it fractures whatever resists its action. The other type is used for throwing projectiles, and must be slower in its action, for otherwise there would be no interval for transmitting motion to the projectile, and the gun would burst. Modern smokeless powder is made from guncotton, but so diluted and grained that its action is slowed down. The projectile will

then begin to move with the first gases formed, and later receive its full motion with the full explosive force of the charge.

The four explosives most discussed are: nitro-glycerine, nitro-cellulose, tri-nitro-toluene, and tri-nitro-phenol, or picric acid.

Nitro-glycerine is not a nitro compound, but a nitrate, a salt of glycerine and nitric acid. Like all these compounds, it is made by treating the raw material with a mixture of nitric and sulphuric acids, the sulphuric acid being used to maintain the strength of the nitric acid. Nitro-glycerine itself is too explosive, and therefore it is usually applied in the form of dynamite, which is made by absorbing the liquid nitro-glycerine in a convenient absorbent, as sawdust or wood pulp, or the fine earthy material called infusorial earth. Different formulæ are used, and the products have different names, as dynamite and forcite, but the essential constituent is nitro-glycerine. The decomposition of nitro-glycerine may be represented by the equation,

$$2C_3H_5(NO_3)_3 = 6CO_2 + 6N + 5H_2O + O$$

The products formed are all gases.

Guncotton, like nitro-glycerine, is a salt, the base being cellulose, which on account of its alcohol groups acts like glycerine. Guncotton has the appearance of the cotton from which it was made, but is heavier and coarser. It burns slowly, and when properly prepared is considered safe. When detonated it explodes violently, even when wet. Pure guncotton is used as a shattering explosive, but when modified and diluted it is the basis of the slow-burning smokeless powders.

Tri-nitro-toluene (T.N.T) has recently come into

great prominence. It shows no vital difference from previously used explosives, but in certain details, as ready fusibility and safety in handling, it has met requirements more satisfactorily. It is a true nitro compound, containing the group, NO_2, and is formed thus:

$$C_7H_8 + 3HONO_2 \rightarrow C_7H_5(NO_2)_3 + 3H_2O$$

It will be noticed that the amount of oxygen is not sufficient for a complete combustion. The practical advantages of this explosive are so marked that it is possible that it will assume an importance in engineering explosives, taking the place of dynamite.

Picric acid, tri-nitro-phenol, $C_6H_2OH(NO_2)_3$, has come into prominence in recent wars. It is a nitro compound, and although less satisfactory than other explosives, it has found considerable application.

It is frequently said that these substances, when lighted, will burn quietly. But for the purpose for which they are to be used a violent action is desired, and they are therefore "detonated," that is, a small charge of fulminating mercury is exploded in close contact. Under these conditions the disintegration takes place with great suddenness and violence. Fulminating mercury is the mercury salt of fulminic acid, $Hg_2O_2N_2C_2$. It decomposes explosively upon being struck or upon application of heat, and, either by the violence of the shock or the nature of the vibration, transmits its decomposing action to the main charge, which then decomposes with equal violence.

CHEMICAL WARFARE

The first gas attack of the war was made with chlorine, the gas which either a chemist or a layman might first select. It is easy to obtain in large amounts, heavy, and exceedingly irritating and

harmful. But the history of gas warfare shows that a substance of such high chemical activity is unideal, as there are readily procurable reagents, such as common soda and the "hypo" of the photographers, which absorb it with the utmost ease. Chlorine may always have a limited application, but the chief war gases must be of another type.

Phosgene, $COCl_2$, was the next gas applied. This is not so conspicuous, and defense against it less easy. A mixture of hexamethylene tetramine $(CH_2)_6N_4$, and sodium phenolate was used at first in the gas masks, and later charcoal in an effective form was developed.

In course of time the gas cloud, that is, the great volume of gas drifting with the wind, was superseded by the gas shell, and after that substances of broader scope could be applied, not necessarily in the form of a gas. The list applied was extended and included substances which have not been common. A few, like benzyl bromide, are in use in laboratory operations and are not considered especially dangerous. Saturating the air with such large amounts of substances is, however, a different matter, and those exposed to such air are incapable of carrying out normal operations, to say the least. Most of the substances in this list of war gases are complex organic compounds. The following are characteristic: Chlorine, bromine, and sulphur trioxide are inorganic. Phosgene, $COCl_2$, may also be considered inorganic, but it is more complex.

Diphenyl chloroarsine, $(C_6H_5)_2AsCl$, sneeze gas
Dichloro diethyl sulphide, $(C_2H_4Cl)_2S$, mustard gas
Benzyl bromide, $C_6H_5CH_2Br$ and xylyl bromide, $C_6H_4.CH_3.CH_2Br$, tear gases.

The organic compounds are selected for their physiological action, and chemically they are too inactive for easy neutralization. Absorption by charcoal was finally settled upon as the defense against them. Mustard gas came to be used more than all others. Its special features are great penetration, and long-continued action. For the last reason it could not be used for all purposes.

Chemical warfare concerns itself with gas attack, gas defense, smoke screens, and any allied work, besides all the other chemical branches which were developed prior to and during the World War.

PAINTS AND VARNISHES

As introduction to this brief discussion, attention may be called to two phases of the subject. The first is illustrated by the use of shellac. Shellac consists of a resinous substance dissolved in alcohol. When this is applied to a surface, the alcohol soon evaporates and leaves the resinous matter spread over the surface in a thin, even, hard layer, which serves the desired purpose. The other illustration is the application of linseed oil. The oil does not evaporate, but absorbs oxygen, and due to oxidation and polymerization, the liquid linseed oil is changed into a solid, sufficiently hard and tough to protect the surface underneath. If to these two ideas we add that of pigments, the whole ground is briefly covered. Pigments are solids, white or colored, which are mixed with linseed oil, making it opaque, and giving it a desired color.

Varnishes may be described as solutions of certain resinous substances in alcohol, turpentine, or linseed oil, so selected and modified that when the mixture is spread over a surface there results presently,

due to evaporation or oxidation, a glossy durable solid. The chemical changes are not altogether clearly understood, though the features already suggested are rather apparent. The resins used, amber, copal, lac, and others, of well-known physical appearance, are of the nature of complex organic acids. However, they are used solely for their physical properties; their chemical nature does not come into consideration. For many of the products in which linseed oil is used, the oil is first boiled. It is heated, often in presence of oxidizing catalyzers, metallic oxides, the practical effect of which is to hasten the oxidation when the oil is later applied. For ordinary paints, linseed oil is not boiled as much as formerly. Paints consist essentially of linseed oil, mixed with a solid to give the paint body, and a pigment in addition, perhaps, to give the desired color. The chemistry of the drying of the oil has already been discussed, and it may be well to discuss the body and pigment, although they are mostly inorganic products. White lead, basic lead carbonate, $Pb_3(CO_3)_2(OH)_2$, is the standard body, although other compounds, such as zinc oxide, barium sulphate and other combinations of zinc and lead, are coming into use. For some purposes these are superior to white lead. Their requirements are durability, fineness, and opacity, which means covering power. When a color other than white is desired, a pigment must be added, and for this purpose colored substances of the greatest variety have been used. Compounds of iron are common, as Venetian red, siennas, ochers, and umbers, all forms of iron oxide. Other metals which furnish colored compounds suitable for pigments are chromium, copper, lead, and cobalt. Organic pigments can be

made in great variety by combining mordants with dyes, and applying the solid substances thus formed. These are less permanent than the inorganic pigments, but serve many special purposes.

ORGANIC ELECTROCHEMISTRY

Inasmuch as organic compounds are as a rule not ionized, and therefore not conductors of electricity, the application of electricity to them must be limited. Yet there are some organic electrochemical achievements, involving the electrolysis of the few organic acids and salts which are electrolytes, and, secondly, the electrolysis of inorganic substances in mixture with the organic, so selected that the products from the former have some desired secondary reaction on the latter. As an illustration of the first case may be taken the electrolysis of sodium acetate, $NaCO_2CH_3$. It is resolved into its two groups, Na^+ and $CO_2CH_3^-$, but the negative group is so complex and so unstable that it at once breaks down to form $CO_2 + CH_3$. But again CH_3 is nonexistent, and two of these units unite to form C_2H_6. There are other reactions of this general type.

The chief reactions of the second type are oxidation, reduction, and halogenation (introduction of chlorine, bromine, and iodine). The electric current is used simply to produce from inorganic electrolytes the oxygen, hydrogen, or halogen necessary to accomplish the action. The main reaction is not new, but the reacting substances are produced more conveniently. Sulphuric acid, for example, produces both hydrogen and oxygen upon electrolysis, and the organic substance is oxidized or reduced according to the pole with which it is brought in contact.

CHAPTER XXIV

THE INORGANIC CHEMICAL INDUSTRIES

THE great realm of inorganic nature is one in which chemical activities have spent themselves. Affinities have had endless time and opportunity to become satisfied and the chemical energy of matter has been dissipated. It is like a clock that has run down. Inorganic chemical industries are impossible until some means are found for winding up the clock again. That is, we must find some source of energy outside this spent matter which may be available for unlocking the combinations made in the course of the ages, thus making available the matter and energy which we desire. These outside sources of energy are not difficult to locate. They make our industries possible, and we should realize that when certain irreplaceable resources are used up, we have spent an asset of fundamental importance. The sources of energy which we now use are of limited number. They are: 1. The energy of the sun stored up in fuel supplies, either of contemporary origin, like the wood of our forests, or of remote origin, like the coal and petroleum supplies. 2. The energy of the sun stored up in the water power of our rivers and streams. It is but natural that we should turn to these sources of energy which are being ever renewed. The growth of electrochemical industries is the outcome of increasing ability to utilize our water power, through hydroelectric installations. 3. A

very few mineral substances are found whose affinities have not been satisfied. Sulphur and metallic sulphides offer the best illustrations of this. Although this energy is ordinarily utilized, it is of little moment in comparison with the vast amount of energy needed in the industries.

It is scientifically proper to note that the unsatisfied affinity of the oxygen of the atmosphere is necessary for the utilization of the energy stored up in the coal. We are so likely to take oxygen for granted, that this fact is not sufficiently appreciated. Oxygen is as truly our source of energy as is the coal which is used for fuel.

When by the preparation of chemically active substances from inert compounds we have established chemical affinities anew, that is, wound up our clock again, we are ready for a second phase of chemical activities. Given active reagents as sulphuric acid, sodium hydroxide, or chlorine, further chemical reactions are in the line of least resistance, and in operations both small and large, they usually present no difficulties. The great problem of chemical industries is the unlocking of the stable combinations as we find them in a spent or burned-out system. A less difficult problem is the application of these unlocked forces to the needs of men. The first is gathering resources together, the second spending them. The organic chemical industries are on the whole in a third class. In these no great sources of energy are stored up, nor yet applied. They are pratically merely fine readjustments of the forms of matter, without the great energy changes of inorganic chemistry.

In spite of the profound and subtle difficulties confronting chemical manufacture, there have been de-

velopments of the industry in the remote past which challenge our admiration. In some fields, glass, ceramics, varnishes, our theoretical knowledge is only beginning to enable us to make improvements. In the end highly developed learning is bound to overtake and pass mere experience in every field; the greater the skill of the empirical industry, the greater will be the accomplishments when it is placed on a scientific basis.

Chemical manufacturing is spreading out in so many directions that only the most conspicuous fields may be profitably discussed. In many of these fields the work of the engineer is all important. In the open-hearth process of steel making, for example, the beautiful chemical manipulation would be impossible without the high temperature obtained by the structure of the furnace. Engineering details must perforce be omitted from our discussion, but any conception of chemical industries would be grossly inadequate if it failed to include the wonderful engineering achievements upon which so often their success depends.

METALLURGY

In the main, the processes of extraction of the metals from their ores must accomplish the solution of two problems. One problem is the proper manipulation of the mass of foreign material, "gangue," which may be mixed with the true ore. In the case of silver and gold the metal is present in exceedingly small proportions, and larger amounts of useless material must be handled. The second problem is the chemical change necessary to convert the compound of the metal as it is found into the free metal, the form in which it is usually desired.

The first problem is solved in various ways. Concentration may be accomplished by hand picking; by driving before a current of water, when the heavier metallic portions are left behind; flotation involves the rising of metallic sulphides with the foam generated by means of certain oils; the magnet is used for the separation of some rich iron ores from material of no value. Fluxing is an almost universal method of disposing of foreign matter when the operation is one at high temperatures. This consists in the proper combination of the foreign matter with other substances so that the whole forms a molten mass, through which the heavy metallic portion will sink and thus accumulate at the bottom. Fluxing is in a sense salt formation of a certain type. If the foreign matter present contains an excess of non-metallic, that is, acid, constituents, as silica, basic fluxes will be added, while if bases as magnesium and calcium oxides predominate, silica would be the flux added. In certain other operations having concentration for their purpose, the metal desired may be converted into compounds soluble in water, so that it may be leached out from the mass of inert rock. This applies to few cases, gold, silver, and copper. Amalgamating gold and silver ores with mercury, so that the mercury settles out with the precious metal in solution is a method akin to this.

The second problem is the proper chemical manipulation of the ores. Ores fall into various groups according to their chemical composition, and each group requires its own proper treatment. The sulphides form one such group, including ores of silver, mercury, lead, copper, arsenic, antimony, zinc, cobalt, and nickel. The essential features of the extraction are two. First, the sulphur must be removed,

which is done by heating with an abundance of oxygen in the form of air. The sulphur burns away, $ZnS + 3O \rightarrow ZnO + SO_2$, forming sulphur dioxide, while the metal, also in combination with oxygen, is left in the residue. The escaping sulphur dioxide is not alone a waste, but a nuisance, as it is destructive to vegetation. Where the conditions are favorable, it is made into sulphuric acid. The residual oxide of the metal is now heated with carbon, usually in the form of coke, and thus its oxygen is removed and the metal obtained free.

Another class of ores is represented by the oxides, including also hydroxides and carbonates. At the high temperature of the operations the hydroxides lose water, and the carbonates lose carbon dioxide, so that each is converted into the oxide. $Cu(OH)_2$, copper hydroxide, $\rightarrow CuO + H_2O$, $CuCO_3$, copper carbonate, $\rightarrow CuO + CO_2$. The oxide is reduced by means of carbon with varying degrees of ease, and carbon monoxide or dioxide is formed according to the conditions. Ores of lead, copper, tin, iron, manganese, chromium, and zinc fall under this head.

Electrolytic methods are becoming important in the obtaining of a number of metals. Aluminium is thus obtained as well as sodium and magnesium. In the first case the actual electrolysis is comparatively simple, the problem being to prepare a suitable raw material. The fundamentals of electrolysis are simple, but the proper control of certain details determines the practical success of the operations.

It must always be remembered that the above descriptions of metallurgical operations are given only in the barest outline. Practically the manipulation is often more complex. The conversion, for example, of a few grams of silver sulphide into pure

silver is performed in the laboratory with the greatest ease. When, however, the operation becomes an industrial one, the handling of large quantities of lean ore, mixed with earthy matter, involving remote regions, and long distances, raising the question of water and fuel supply, the cost of labor and necessities, the ease of the chemical transformation becomes a comparatively small portion of the whole. Engineering and economical questions often quite overshadow it.

In addition to the first great step, the extraction of the metals from their ores, methods of refining are often required, and further manipulations needed. Copper and lead are cases in hand of metals which must be further treated in order to give them the required purity. In both cases the more valuable silver may be present as impurity, and its recovery is a partial compensation for the operation. In such refining the details are too varied for a general statement; yet one important principle often applies, namely, the oxidation of a more active impurity. If copper containing iron, sulphur, and other active elements is melted and treated with air, these more active elements oxidize, and rising to the surface of the heavy metal may readily be removed. Silver is "parted" from gold by treatment with hot sulphuric acid, in which the silver is soluble.

Another general principle of refining is the electrolytic method, described in another place. This is of great effectiveness, inasmuch as in one step of the process, the metal in hand is freed from all the less active metals, and in the other step, from those which are more active.

Among the further operations to which metals are submitted, are alloying, plating, and the various

A NUGGET OF SOLID COPPER IN A MICHIGAN MINE

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COCKPIT OF THE DIRIGIBLE C-7, FIRST AIRSHIP IN THE WORLD TO BE LIFTED BY THE NONINFLAMMABLE HELIUM GAS. NO ONE WOULD BE ALLOWED TO SMOKE IF THE BALLOON WERE FILLED WITH HYDROGEN

changes involved in iron and steel. Copper is probably applied the most in making alloys. Zinc, lead, tin, nickel, antimony, and aluminum are used also in making brass, bronzes, German silver, type metal, coinage, and other much-used alloys. Alloys of chromium, as nichrome, are of great use in electric heating devices. Tin plating and galvanizing of iron are similar operations, the former consuming a large portion of the tin available.

The iron and steel industries in great part are applications of mechanical appliances for shaping the metal in the desired forms. Such are the foundries, the forges and the rolling mills. But preceding each application of a given form of metal is the chemical transformation needed to give it the desired properties. Such transformations have been discussed in a brief way under iron and involve the addition or substraction of other elements. In connection with the complicated structure, both chemical and physical, of the many forms of iron and steel now in use, as well as of other metals, the science of metallography has grown up. It is the study of the relation to each other of the various elements in the formation of compounds, and of the various compounds present in the formation of more complex mixtures, the whole making up what we call iron and steel. The resources of chemistry are supplemented by the microscope. A smooth surface of the metal is treated with an active reagent, as iodine. This dissolves some portions of the complex mass leaving others in such pronounced shapes that it is possible to derive information from the microscopic examination. Among the substances identified in these mixtures are the following: ferrite, pure iron; graphite, carbon; cementite, Fe_3C, an iron carbide;

perlite, an alloy of cementite and ferrite; martensite, a solution in varying proportions of carbon in iron.

NONMETALS

A number of the nonmetallic elements are in such demand that their preparation has become an industry of some magnitude. Oxygen is used medicinally, and for obtaining high temperatures, as in welding. Electrolysis of water is one source of commercial oxygen, the hydrogen often being wasted, while another source is liquid air, from which the more volatile nitrogen is allowed to escape (and wasted) until the proportion of oxygen is sufficient to make it effective. When nitrogen fixation through the synthesis of ammonia becomes established this nitrogen may find an application.

Chlorine is manufactured in increasing amounts, and finds application in bleaching textiles and in disinfecting water supplies. The old method of freeing the chlorine from hydrochloric acid by oxygen in some form is now supplemented by the electrolytic methods. Liquid chlorine is frequently prepared and marketed as such, but much of it is still converted into bleaching powder, $CaOCl_2$, which is efficient either for bleaching or for disinfecting. Bromine and iodine may be liberated by similar methods, and all that is produced finds a market. Other nonmetals are either found native, as sulphur, or prepared in quantities demanded by the industries. The various forms of carbon, lampblack, coke, charcoal, and graphite are prepared in great quantities. Phosphorus is the basis of the match industry, boron and silicon are used for special purposes; but details beyond those already given must be omitted.

Salts and brines supply a number of substances in addition to common salt. Common salt is obtained chiefly by means of artificial brines, formed by forcing water to the subterranean deposits, and drawing out and evaporating the solution there formed. Salt supplies most of the chlorine and sodium required by the industries. Evaporation of concentrated surface brines, as sea water and the Great Salt Lake water, is also profitably practiced. From deposits of solid salts there are obtained sodium nitrate, the potash and magnesium salts of the German deposits, borax and soda. Salts in solution yield many products, conspicuous being the potash of the West, which so far, unfortunately, has been obtained in quantities too small to supplant the supplies from overseas.

THE ACID INDUSTRIES

The great acid industry is based, in the first place, upon the manufacture of sulphuric acid by making a combination of the constituent elements. From this finished product the other acids desired are made by a simple double decomposition reaction. The making of sulphuric acid has already been described. The steps are: sulphur in any available form, to sulphur dioxide, to sulphur trioxide, to sulphuric acid. Further steps in the making of acids are simple, provided the raw material is available. Salt and sodium nitrate are easily converted into their corresponding acids by mixing them with sulphuric acid and heating. The new product is more volatile than the sulphuric acid and may readily be separated from the mixture. The gaseous hydrochloric acid is absorbed in vertical towers by coming in contact with a descending stream of water; the nitric acid being a liquid, is simply condensed. Other

acids do not compare with these three in importance, but they may be prepared, given the necessary salt, with equal facility. Carbon dioxide, so much used for beverages, being an acid oxide, is prepared from calcium or magnesium carbonate by this method. The choice of these is decided by the value of the by-product.

THE ALKALI INDUSTRIES

Just as there is a group of acid industries closely correlated, so there is a group of alkali industries. Before the modern development of industrial chemistry the basis of this was the making of lime from limestone. By mere heat calcium carbonate, an abundant mineral, can be converted into calcium oxide, this into the hydroxide, and thus an active base obtained. This is convertible into the other active bases, sodium or potassium hydroxide or ammonia, in a way comparable with the conversion of sulphuric acid into other acids. This was the operation followed in the olden days when wood ashes were made into lye by treatment with lime.

Historically the great problem of the alkali industry has been the manufacture of sodium carbonate. Descriptions of the old Leblanc process and the modern Solvay process fill many pages of an industrial chemistry. The problem is a difficult one, for we are trying to make a reactive substance, sodium carbonate, with energy stored up, out of an inactive compound, common salt, whose affinities have all been satisfied and their energy dissipated. Stated otherwise, it means removing from the sodium the very active chlorine, and replacing it by the less active carbonate group. The old Leblanc process made use of such changes and reagents as were available and which brought the final result. Its

features are the conversion of sodium chloride, salt, into sodium sulphate, by means of sulphuric acid. The sodium sulphate is then heated with carbon, and converted into a less stable sulphide, this in its turn is converted into the carbonate by heating with calcium carbonate.

The first step is the conversion of the very stable sodium chloride to the more complex and therefore more readily decomposable sulphate. The second step makes use of the energy of carbon to move the product from the stable nonreactive into the unstable class, in which form it is capable of final conversion. Two by-products are of importance. The hydrochloric acid was at first found a nuisance, but with the development of chlorine bleaching methods it became an asset. The calcium sulphide by-product is not alone an objectionable substance, when it is left to oxidize, but it represents a loss of all the sulphur of the original sulphuric acid. Hence methods have been devised for its treatment for the recovery of sulphur.

The Solvay or ammonia-soda process has steadily increased in popularity. Its main reaction is $NaCl + NH_4.H.CO_3 \rightarrow NaHCO_3 + NH_4Cl$. This is merely a double decomposition reaction of the usual type, based upon the comparatively low solubility of the sodium hydrogen carbonate, and involves no important energy changes. Energy changes are involved in the preparation of the ammonium hydrogen carbonate, $NH_4\ H\ CO_3 (NH_3 + H_2O + CO_2)$, which requires the preliminary release of the ammonia from ammonium chloride,

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + H_2O + CaCl_2.$$

Applications of energy from without, requiring the use of fuel, are in the formation of the calcium hy-

droxide from limestone, and the conversion of the resultant $NaHCO_3$, baking soda, into the sodium carbonate. The by-products, ammonia and carbon dioxide, are used in further operations; but chlorine and calcium are wasted.

The efficiency of this process depends upon the skillful application of engineering principles in the designing of the apparatus. With laboratory apparatus it is not easy to carry out the process. Yet through proper design of machinery, it is made a basic chemical industry.

It is to be noticed that baking soda, $NaHCO_3$, is the first product made by the Solvay process. It is used in large amounts for baking powder, but its chief application is for conversion into the normal carbonate.

Sodium hydroxide, caustic soda, also called lye, is made from the carbonate by double decomposition with lime, that is, calcium hydroxide. Electrolytic methods have assumed a large place in the manufacture of sodium hydroxide.

FERTILIZER INDUSTRIES

These industries have several main divisions, potash, phosphate, and nitrogen, including the utilization of any organic residue which the waste of our civilization may supply.

The term potash indicates, when used exactly, the oxide, K_2O, but is applied to any compound in which the potassium is in available form. The great bulk of that produced is used for fertilizer purposes, 90 per cent before the war. At that time practically all came from the Stassfurt deposits. These deposits were formed by the evaporation of sea water, under unique conditions, so that all its constituents were

left in place. Sea water contains 78 per cent of sodium salts and only 4 per cent of potassium salts. The latter are very soluble, so that in the evaporation of sea water the small proportion of potassium salts is usually either never deposited or removed by solution after deposition. With the war the German supplies were stopped, and we have since been looking eagerly for new sources. The deposits in Alsace are much talked of, but we are most interested in American sources. Certain lakes of western Nebraska, Searles Lake of California, and the seaweeds of the Pacific coast have produced potash to the extent of about one-fourth of the amounts required. The supply from the extreme West requires long transportation to reach the agricultural centers of the country. Other sources looked to are cement kiln dust, blast furnace dust and the limited supplies from wood ashes and sugar residues.

In the solid crust of the earth the potassium is as abundant as the sodium. As the rock disintegrates, the potassium is retained by the soil, while the sodium passes on to the sea, hence the disparity of proportions there. The potassium in primary rock is held in such stable combination that so far no method has been devised for its profitable extraction. We must look to the concentration of geological ages for our supplies, and so far the search in America has been only partly successful.

The phosphate industry is a simple one. It happens that in some of the South Atlantic States calcium phosphate occurs in abundance. This phosphate is in a form so insoluble that plants cannot utilize it. It is therefore ground fine and mixed with sulphuric acid, when the following reaction takes place:

$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow CaH_4(PO_4)_2 + 2CaSO_4$. Both of the products are slightly soluble and are valuable as fertilizers. Other forms of phosphate worked up for fertilizers are the bone products, for bone is mainly calcium phosphate, and the phosphate slags of steel making, obtained in the linings of steel converters when the iron is rich in phosphorus.

Nitrogen fixation was discussed in the chapter on nitrogen. For agricultural purposes, most nitrogen compounds will serve the purpose of supplying the plants with that element, because in the end nitrogen in any combined form is oxidized to the nitrates necessary for plants. Industrially nitrogen is supplied to agriculture in several forms. Ammonium salts are obtained from the products of soft coal distillation. Sodium nitrate is obtained from the niter beds of Chile. Any nitrogenous refuse such as slaughterhouse waste or garbage residue may be used as such or mixed with other substances of fertilizer value.

CEMENT, GLASS, POTTERY

Portland cement is an artificial combination of limestone and clay which is highly heated and then ground to a fine powder. The proportions were determined in the first place by natural mixtures found to give the desired results. Cement may be called a mixture of calcium silicate and calcium aluminate. Its setting when mixed with water is difficult to explain, but is said to be due to hydrolysis of these salts, followed by recombinations between the bases and acids present and of these new salts with water.

Glass.—The making of glass, as well as that of pottery, is an ancient industry, developed to a high degree of perfection before the age of theoretical

knowledge. They are both silicate industries, involving the combination of silicon dioxide with one or more bases, the combination being fusible according to its complexity. These are then of the nature of salts.

Glass in its common form is a mixture of silicates of calcium and sodium. Its complex nature causes a delayed crystallization (glass is often called a supercooled liquid) giving the glass two of its chief virtues, transparency and the property of softening before melting. Other virtues of glass are insolubility and general inactivity toward reagents. Glass is made by fusing together sodium carbonate or sulphate, calcium carbonate, and sand. The nonmetallic oxides of carbon and sulphur in combination with the bases are expelled in the process of heating. While this soda-lime glass serves many purposes, it is nevertheless too susceptible to sudden changes of temperature and the solvent action of water and alkalies. Hence other oxides are introduced, and the result is an improvement. Bohemian glass contains potassium in place of sodium, Jena normal glass contains zinc and aluminium oxides. Several other metallic oxides are applied as well as the nonmetallic oxides of boron and phosphorus. Lead glass is noteworthy in that it is brilliant but very soft.

Glass must be annealed, that is, cooled with care, so that the interior may not be left in a state of tension. The Prince Rupert drop illustrates this state of tension in an exaggerated degree. These drops are made by sudden cooling of molten glass. If the small end of the drop is broken off, it causes the whole to fly into pieces with almost explosive violence.

The coloring of glass is accomplished in one of two ways. Certain substances, insoluble in the glass, are mixed with the mass. They remain diffused in a very even manner and give an effect of color or milkiness. Ruby glass is colored by very fine particles of gold or cuprous oxide. Milk glass contains such substances as tin and zinc oxides, which are suspended through the glass and render it opaque. Other effects are produced by the introduction of metallic oxides which form true colored compounds with the silica. These compounds are evenly diffused through the entire mass. Among the most striking is the compound formed with cobalt oxide, which is of an intense and beautiful blue color.

Pottery.—Clay is a hydrated silicate of aluminium, possessing the property of plasticity when moist, and capable of burning to a hard mass, which, in that it does not actually fuse, retains the shape given while soft. Ordinary brick and the crude forms of earthenware represent this plainly. The burning, or adherence of the clay particles is probably due to a very superficial melting of fine projections and foreign substances. The article, though it shrinks, retains its shape, and unless heated very hot is porous. When the article is designed for impermeability to water, it is glazed. This glaze consists of feldspar and other silicates which are applied to the article in the form of a thin layer. On account of their greater complexity, they are more fusible than the original clay, and when the article is fired again, this layer melts over the whole surface, making a watertight glaze. The various grades of pottery vary according to the purity of the materials and the manner of mixing. When the glaze is diffused throughout the original clay, the whole mass is more

fusible, requiring more delicate handling, but the product is translucent and attractive. This is often called china, while the name porcelain is applied to less translucent ware, glazed on the exterior, but opaque within. This glaze can be colored after the manner of glass. The design in the proper material is placed on the ware before or after applying the glaze, the former giving the more permanent result.

ELECTROCHEMICAL PROCESSES

The present era is justly criticized because of its inattention to the conservation of our natural resources. Coal, the usual source of energy, is being consumed at an increasing rate as our industries grow. Coal deposits are among the natural resources which, once used, are irreplaceable. Hence we may feel gratified that economic pressure is resulting in the utilization of water power in increasing measure, with consequent saving of coal. Such power is conveniently converted into electrical power, which in its turn is available for chemical manufacturing purposes in two ways quite independent of each other. One of these makes use of the electricity merely as a convenient source of heat, while the other is strictly electrochemical, depending altogether on the special relations between chemistry and electricity.

In the former set of operations the electric furnace is applied. In this the heat is developed either after the manner of arc lights, or by the resistance of the mass of material through which the current flows, illustrated by our domestic electric heating devices. Steel, graphite, carborundum, silicon, calcium carbide and carbon disulphide are products of such furnaces. In them the use of electricity is

solely as a source of heat, which is applied to greater advantage, both technically and economically, than when produced by the combustion of coal.

The second set of operations involves actual electrochemical changes. Such operations are: A, electroplating; B, electrorefining and the recovery of metals from wastes; C, the preparation of certain metals as sodium and aluminium; D, the preparation of secondary products like sodium hydroxide; E, the electroorganic industries, discussed in another chapter.

The first principle of all these operations is a simple electrolytic separation of the positive and negative constituents of a suitable electrolyte. In some cases this is the end of the process, as when aluminium is obtained, or silver is plated on a brass object. In other cases complications ensue, as when sodium is liberated in presence of water. Then the complication must be avoided by proper contrivances; or, on the other hand, advantage may be taken of this secondary reaction. When sodium chloride is electrolized, there are three possibilities. Sodium and chlorine may be desired, in which case the sodium must be prevented from reacting with chlorine or oxygen. If sodium hydroxide is wanted, the arrangement is such that sodium may react with water, but not with the chlorine. When sodium hypochlorite is the object, the resulting sodium hydroxide and chlorine must be brought together, but other possibilities prevented. Many details are of great moment. The intensity of the current, the nature of the electrolyte, the nature and size of the electrodes, and contrivances for separation or uniting the products of the electrolysis are among the features which require careful regulation.

CHAPTER XXV

INORGANIC ANALYTICAL CHEMISTRY

A PRACTICAL study of chemistry very promptly develops a need for methods of testing and analyzing the substances with which we deal. Some of the simpler tests are used with great frequency, as the litmus test for acid and alkali, the silver nitrate test for hydrochloric acid and chlorides, and the barium chloride test for the sulphate group. In any given case we recognize a substance by manipulating it so that some very characteristic property will become apparent, most frequently one that is recognized by the appearance, less frequently by the odor, and still less often by the application of one of the other senses. The theory and technique of these specific tests, with the study of separation and distinguishing the several members of a mixture, is the study of "Qualitative Analysis." When the operations are so modified that, in addition to the nature of the substances present, their quantities and the percentage composition of the whole are established, the study is "Quantitative Analysis."

It will not be profitable to attempt to give the whole scheme of qualitative analysis, but enough may be shown to illustrate the logical orderliness of the procedure.

Inorganic substances which we usually meet with are of comparatively few types. They may be in the form of elements, or they may be compounds.

The latter are not likely to present any great variety. The compounds may be compounds with hydrogen or oxygen, or they may be in the form of acids, bases, or salts. Recognition is most readily accomplished by identifying first the metal present, and then the nonmetal or the nonmetallic group. A number of elements, as chlorine, bromine, iodine, carbon, and sulphur have such striking properties that they are easily identified as elements. But the metals are so much alike in their external properties that it is more convenient to convert them into salts, and to make our tests upon these. Qualitative analysis deals chiefly with the elements in the form of soluble compounds, and its tests are then not so much for the elements themselves as for the positive metal ions, on the one hand, and for the negative nonmetal ions on the other. The common test for silver, for example, is not a test for silver as metal, but for silver in the form of an ion. If we wish to find what metals are present in a silver coin, we first dissolve the coin in nitric acid, when the metals present will be converted into soluble nitrates. To the solution of these products in water we add a little hydrochloric acid. The negative chlorine ions of the latter unite with the positive silver ions present, forming a characteristic insoluble silver chloride. From its appearance and other tests applied, we are certain that this is silver chloride, and therefore know that there was silver in the original coin. Other metals, as copper, will not respond to this test. If we now remove all the silver ions by the means just discussed, and add ammonia to the rest, a striking blue color is developed. This is due to the presence of copper ions, and we know that the coin contained copper as well as silver. It is cus-

tomary to speak of silver and copper and other metals as being present in a solution. This is inaccurate and allowable only by convention. In the solutions we have the salts and consequently the ions of silver and copper and other metals, and our tests are usually for these ions.

It may be assumed that each ion has its own characteristic tests. Those for silver and copper have been mentioned. Just as the chlorine ion is a test for the silver ion, so the silver ion is a test for the chlorine ion. Most tests are thus used in two ways. Barium ions and sulphate ions form a much used pair of mutually reacting ions. That is, barium ions form with sulphate ions a characteristic precipitate which serves for the identification of both. The identification of a pure substance is a very easy matter, and may be accomplished in a few minutes. When, however, several substances are mixed, the problem becomes complex and the various tests must be reduced to a system. This system is to be described briefly.

The metals usually met with, either as metals or in their compounds, number about twenty. They will be arranged in the groups into which they fall according to the analytical scheme. This conforms roughly to the electromotive list, reversed, and is based upon the nature of the compounds which these metals form with the various reagents. In the classification and discussion many details will be omitted.

Group I.	Silver, and mercurous mercury.
Group II.	Copper, lead, mercuric mercury, cadmium, bismuth, tin, antimony and arsenic.
Group III.	Iron, aluminium, and chromium.
Group IV.	Zinc, cobalt, nickel, and manganese.
Group V.	Calcium, strontium, barium, and magnesium.
Group VI.	Sodium, potassium, lithium, and ammonium.

If the substances which are engaging our attention are not in solution in water, they are converted into soluble compounds by proper treatment. In a few cases this is not possible and the tests are carried out along other lines. Ordinarily, however, the scheme here given applies completely.

Let us assume a mixture containing all these metals in solution in water, in the form of salts. If to this complex mixture we add hydrochloric acid, HCl, the chlorine ions will form insoluble chlorides with a limited number of the metals. These chlorides will settle out and may be filtered off. The solid collected on the filter paper will consist of the chlorides of silver and mercurous mercury, while in the clear liquid running through will be included all the other metals of the list. We therefore say that silver and mercurous mercury are the metals of group I, and that hydochloric acid is the group reagent.

To the clear solution containing all the other metals, as well as some of the hydrochloric acid added as above, a sufficient amount of gaseous hydrogen sulphide, H_2S, is added. This will form insoluble precipitates with the metals designated as group II, and the precipitates may be collected on a filter paper. All the remaining metals will be found in the clear solution running through. Hydrogen sulphide therefore is the group reagent for the metals of group II.

Before proceeding further, any hydrogen sulphide remaining in the solution must be removed by boiling, and then the reagent for group III may be added. This is ammonia, or ammonium hydroxide, NH_4OH, which forms precipitates of insoluble hydroxides of the three metals. As before these may

be collected on a filter, and the clear filtrate will contain the remaining metals.

The group reagent for the next group is ammonium sulphide $(NH_4)_2S$. When the precipitate thus formed is removed, the solution is ready for the group reagent of group V, namely, ammonium carbonate. The procedure is here the same as in every previous case.

There is no convenient substance which forms insoluble compounds with the metals of group VI. From any ammonium compound the ammonia with its characteristic odor is easily obtained, but for the others the identification is not so easy.

The scheme of analysis continues in that now it is necessary to establish tests to identify one metal of a group in distinction from the others of the same group. This is not difficult, provided there is only the one metal present, for each metal has one or more reactions so characteristic that it may be identified with certainty. When two or more metals of the same group are mixed, the problem is greatly complicated and various methods must be applied for separating them before each may be identified. The details of these operations are very important, but for our purpose they may be omitted entirely.

The metals of the sodium group do not form characteristic precipitates, and their identification in mixtures is surprisingly difficult. The flame color and the spectroscope are helpful, for these metals give striking colors to the Bunsen flame.

The nonmetallic radicals, or ions, are grouped after the same manner as are the metals. There are fewer such ions, and they are more promptly recognized, so that they present fewer difficulties than do

the metals. The classification of the most important negative ions is as follows:

Group I.	Chlorine, bromine, and iodine. Group reagent, silver nitrate in presence of nitric acid.
Group II.	Sulphate SO_4, sulphite SO_3, carbonate CO_3, borate B_4O_7, phosphate PO_4. Group reagent, barium chloride in neutral solution.
Group III.	Nitrate NO_3, nitrite NO_2, chlorate ClO_3. There is no group reagent.

As with the metals, after the group in which a negative ion belongs has been established, special tests are required to determine the particular members of the group. Most of them show such striking reactions that the matter is comparatively simple. For example, in group I, the free halogens may be liberated and easily recognized.

Having established the positive and negative ions which may be present, we may assume that our problem has been solved. These ions may be put together according to certain probabilities, but there is often uncertainty as to what combinations were originally present in a mixture, and the question is best left unanswered.

This résumé of the plan of qualitative analysis is exceedingly brief and superficial. A little practical experience would soon show how the scheme works out. There are many special problems and complications and some abbreviations. Blow-pipe analysis, used much less now than formerly, is often a convenient supplement to the above methods.

The microscope promises many improvements on the methods outlined, and some extension of its scope. As we ordinarily obtain a precipitate, we can

judge of it only by its gross features, color, and general appearance, as crystalline or gelatinous. Under the microscope small crystals ordinarily indistinguishable from others show their characteristic crystalline form. The shape, size, and some optical properties of the crystals are easily determined. The reliability of the conclusions, the observation of added characteristics and the small amounts needed, all unite in making the microscope useful in this particular field of chemistry.

Quantitative analysis is the study of the theory and technique for the determination of the amounts of the different constituents of any substance. The processes must be conducted with great care and are very time-consuming. For special purposes there are many excellent shortened methods, but, on the whole, the work requires time and deliberation. There are two sets of methods used, those in which the substances involved are weighed, called gravimetric analysis, and those in which the volumes of the solutions of substances used are measured, called volumetric analysis. The latter methods are usually much more rapid, and in some cases are very accurate. But their application is often impossible. To give some impression of the scope of each, concrete illustrations will be given.

Let the problem be to determine the proportion of silver present in the metal used in a silver coin. A bit of the metal is weighed. The amounts used in gravimetric analysis are very small, as care and accuracy are thereby greatly aided. Two or three-tenths of a gram would be ample for the cases in hand. The sample is then dissolved in nitric acid, that is, the silver and any other metals present are converted into the corresponding nitrates. Every

precaution is used throughout to prevent loss. When the metal is all dissolved the solution is diluted with water and hydrochloric acid is added. The silver forms an insoluble precipitate with the chlorine, which, after being stirred and warmed, collects in an easily handled mass. There is now prepared a filter of finely divided asbestos, like a layer of paper, over the perforated bottom of a crucible. This is weighed after careful preparation and drying. When the solution containing the silver chloride is poured out upon this filter, all soluble matter runs through with the water, and the silver chloride is left in the crucible. This is carefully washed, dried, and weighed. From the weight of silver chloride the amount of the silver can be readily calculated by the proportion,

$$\frac{\text{Known weight of silver chloride}}{\text{Wanted weight of silver}} = \frac{AgCl}{Ag} = \frac{\text{Mol. Wt. of AgCl}}{\text{Atom. Wt. of Ag}} = \frac{143.4}{107.9}$$

The comparison of the amount of silver present to the whole metal may now be made.

This operation is repeated in its main features for most gravimetric determinations. The sample under investigation must be weighed and brought into solution. To this solution a reagent is added which forms a new compound with the part under discussion, separable and weighable with accuracy. The methods by which these conditions are fulfilled form the technique of analytical chemistry.

Volumetric analysis applies frequently to the determination of acids and alkalis, although its extension to other substances is considerable. One or two characteristic processes or methods will be explained. The methods are based upon the use of

solutions of substances of known concentration, and the work is simplified if these are made up of a certain normality, for example, tenth normal. If all solutions used were tenth normal, then the volumes applied would always bear a simple relation to each other. As the preparation of solutions of an exact concentration is a very considerable trouble, it is more profitable to make them of approximately the desired concentration, then to determine the error and apply the correction arithmetically.

Let us take for an example the determination of the amount of acid—we will call it acetic acid—in vinegar. We will measure out with great accuracy, by the use of a pipette, 10 c.c. of the sample. This is placed in a beaker with a convenient amount of water. There is now added an indicator, like litmus, though there are other better ones, which will tell when all the acid has been neutralized by the addition of the base. From a graduated burette, set at 0, there is now allowed to run into the vinegar, with constant mixing, a solution of sodium hydroxide of known strength, until the indicator tells us that the acid is just neutralized. If we now take the reading on the burette, it will tell us how much of the sodium hydroxide was required, and from this a simple calculation will tell us the amount of acid in the vinegar.

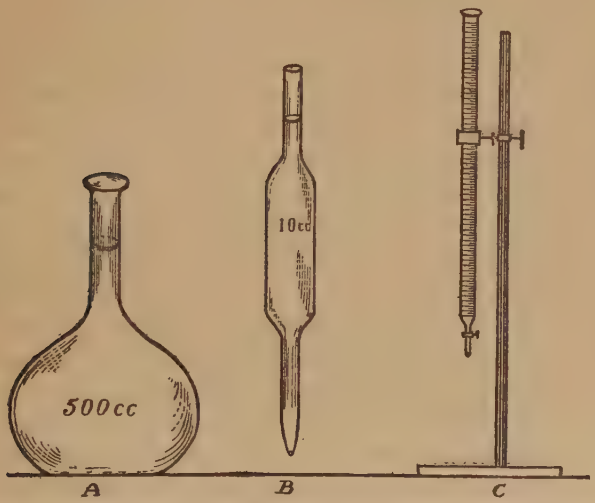
This method applies especially to the balancing of acid and basic solutions, but is of extensive application in other ways. A number of typical illustrations of other methods could be given, but they are of very technical nature, and follow out the same ideas as that already explained. These methods usually depend upon the ready determination of the end point, that is the moment when just enough of

the second solution has been added to react exactly with the first solution. Indicators, like litmus, phenolphthalein and others, show by the change of color that the acid and base just neutralize each other. Iodine is a very common reagent in these operations, as it combines a ready activity with a striking color effect when starch is present. That is, if iodine solution of a known concentration is added to certain solutions, a little boiled starch being present, these substances will combine with the iodine until they are completely used up. One drop of iodine solution in excess will then develop a strong blue color with the starch. Potassium permanganate solution is another useful reagent. It has the double virtue of supplying oxygen, and of losing its striking color as long as it is losing this oxygen. The moment the substance being treated fails to assimilate more oxygen, that moment the color of the permanganate remains and the result is apparent. There are other color changes which are useful for these determinations. By proper manipulation, a method may be varied and so lend itself to a number of useful applications.

The volumes, which are the essential features of this type of analysis, are determined mostly by three pieces of measuring apparatus, the pipette, the burette, and the measuring flask. The graduations must be made with great care. The pipette, in sizes from 1 to 100 c.c., and the measuring flask, in sizes from 25 to 2,000 c.c., can be used only for the stated amounts. The burette, on the other hand, is used to deliver any required amount, and the amount required is then read off.

Electrochemical analysis may be mentioned as an application of electrical methods to the shortening

and refining of the methods of analytical chemistry. The principle involved is simple enough. If a solution containing copper is placed in a platinum dish which is connected with the negative pole of a battery, all the copper will presently be deposited upon the dish, and, after proper washing and drying, the



THE MOST COMMONLY USED VOLUMETRIC APPARATUS

A, the measuring or graduated flask; B, the pipette; C, the burette.

weight may be taken and so the amount of copper present known. This method applies to other metals as well. A limited number of metals in the form of higher oxides may be caused to deposit upon the positive electrode of the battery, for example, manganese as the dioxide. This is too active as a metal to be deposited upon the negative pole as in the case of copper.

CHAPTER XXVI

PHYSICAL CHEMISTRY

PHYSICAL chemistry concerns itself with the chemical interpretation of the physical constants of substances. The determination of these values requires the adoption of physical methods to such an extent that the work takes on a nonchemical aspect, and one often hears the expression "the borderland between physics and chemistry." The results obtained from these studies have often led to generalizations from which the theories underlying the subject of chemistry have been developed. The dependence of numerous chemical conclusions upon such data will be pointed out in the sequel. Even when physicochemical measurements have not yet led to important generalizations, they have served many useful purposes in less important respects. The knowledge of specific gravity of solutions has not been reduced to important laws or theoretical conceptions, but in the way of analysis and practical convenience it is of the greatest service. On the other hand, certain measurements connected with solutions have led to the theory of ionization, which has helped to solve so many problems of chemistry.

In an ordinary study of descriptive, or general chemistry, we assume certain generalizations and theories as established. Such are the gas laws, and the molecular and atomic theories. By means of these we can comprehend the phenomena of chemis-

try as parts of a whole and we can summarize our experience of the past and prepare for future developments. It is the work of physical chemistry to acquire the necessary data by careful measurements, and from them to derive the laws and theories by which we weave the whole together. Even a brief consideration of general chemistry is incomplete without some physical chemistry, and of the twenty-one chapters here devoted to the subject of general chemistry, five are taken up mainly with physical chemistry. Physical chemistry, however, is too extensive a subject to be thus incidentally included. The following brief discussion can hardly do more than indicate the more outstanding lines of interest and to show how intimately and usefully they are associated with our comprehension of chemistry.

THE SOLID, LIQUID, AND GASEOUS STATE

The physical state, superficially considered, is but an external feature in connection with elements and compounds. The nonmetals all form acids, regardless as to whether they are solids like sulphur or gases like nitrogen. When, however, definite comparisons can be established, the subject of physical state at once becomes interesting and instructive. Chlorine, bromine, and iodine, as will perhaps be recalled, are three elements of great similarity. They are of striking physical properties, all very active chemically, and they form salts of remarkable similarity. The differences which they exhibit are differences in degree, and the physical state is a very apparent index of this difference. Chlorine is a gas, bromine a liquid, and iodine is a solid. The atomic weights, 35.5, 80, and 127, respectively, show

an arithmetic relation bearing out the first suggestion of the solid, liquid, and gaseous state. The chemical properties also follow in order, as do the physical properties. Here there is a close relationship between the variation in the physical state and the variations in other properties, both physical and chemical.

In the series of organic compounds, as the hydrocarbons, alcohols, and acids, changes in the physical state follow very closely upon the increasing complexity of the molecule. CH_4 is a gas, C_6H_{14} is a liquid, and $C_{20}H_{42}$ is a solid. The simplest alcohols, methyl, and ethyl, CH_3OH and C_2H_5OH, are liquids, but those containing a large number of carbon and hydrogen atoms, as $C_{18}H_{35}OH$, are solids. The same is in a general way true of the acids and all other organic compounds. These facts are of profound significance in the field of biochemistry. Tissue must be solid on the whole, and yet must be built up of the elements carbon, hydrogen, oxygen, and nitrogen. The difference in the physical state and other physical properties connected with the structure of the molecule results in insoluble solid compounds when the molecule is complex, and soluble solid, liquid, or even gaseous compounds when the molecules made up of the same kinds of atoms are simple, each state serving the special needs of the animal organism.

THE BOILING POINT AND MELTING (FREEZING) POINT

The melting point of solids and the boiling point of liquids are but phases of the subject of physical state. A solid melts easily, or passes to a gas easily, other things being equal, when it has a simple mole-

cule. The boiling point of each alcohol of a series is higher than that of the one before with some semblance of regularity. The boiling point of any substance, moreover, is associated with its chemical structure. The influence of a hydroxyl group (—OH) for example, is to raise the boiling point about 100° C. Propyl alcohol, C_3H_7OH, a monohydroxy derivative, boils at 97° C. The dihydroxy derivative, propylene glycol, $C_3H_6(OH)_2$ boils at 188° C., while glycerine, the trihydroxy derivative, $C_3H_5(OH)_3$, boils at 290° C.

The influence of any substance upon the boiling point or freezing point of another in which it is dissolved is so regular that it has been of very great use in determining the composition of chemical substances. In a rough way these facts are commonly appreciated. In candy making, the determination of the boiling point of the sirup indicates the composition of the sugar solution. It is well known that the presence of alcohol or some other substance lowers the freezing point of water to such an extent that it may be kept from freezing in automobile radiators. This influence of different solutes on the solvent is regular, determined, however, not by the number of grams of the substance dissolved, but by the number of the molecules. One gram of ordinary alcohol, molecular weight 46, contains over seven times as many molecules as one gram of cane sugar, molecular weight 342. To obtain equal effects for the two substances they must be introduced in the proportions of 46 parts of the alcohol, or 342 parts of the sugar in equal amounts of water; these proportions contain equal numbers of molecules. The use of ordinary alcohol for this purpose is so common that it may be interesting to apply the

formula which expresses this general relation. The formula, modified for the sake of compactness is:

$$\text{Depression of freezing point in degrees, F.} = \frac{3400 \times \text{alcohol per cent.}}{46 \times \text{water per cent.}}$$

The number 3400 is a so-called constant, correct only for water. For other liquids it has another value. 46 is the molecular weight of the alcohol. For 5, 10, 20, and 30 per cent alcohol we may very readily compute the lowering of the freezing point, which will be found to be 4°, 8°, 14°, and 32° F., respectively. The same method of calculation would apply to any other usable substance.

A simple reversal of the formula will permit us to determine molecular weights from the experimental determination of the freezing point depression. This experiment is a very common one. A small amount of the substance under discussion is weighed and added to a known weight of the solvent. For this purpose water is only exceptionally adapted. The mixture is cooled carefully, being stirred all the while, and a thermometer of very special construction, reading to 1/100th of a degree is used to measure the lowering of the freezing point. The apparatus and operation for boiling point elevation is very similar. The constant used varies for different solvents and is also different in each case for the boiling point and freezing point determination.

When the methods just outlined were applied to acids, bases, and salts dissolved in water, the results obtained did not conform to the theoretical values. The effect was always greater than the calculation called for. In the end, these deviations have led to the development and adoption of the theory of ionization, discussed in a previous chapter. Accord-

ing to our conception of ionization, a salt like sodium chloride, dissolved in water, yields two ions, Na^+ and Cl^-. The influence upon the boiling point and freezing point is determined, not by the one unit, or molecule, of sodium chloride supposedly present, but by the two units, the ions formed when the salt dissolves in water. A salt like barium chloride, $BaCl_2$, has an even greater effect, inasmuch as it is dissociated into three ions, Ba^{++} and $2Cl^-$. The conclusions thus established are confirmed by the study of the conductivity of solutions, a branch of electrochemistry.

THE SPECTROSCOPE

The spectroscope is a physical instrument which lends itself to the solution of chemical problems in a unique manner. Reference has already been made to the fact that potassium and sodium compounds color the Bunsen flame violet and yellow, respectively. Lithium colors the flame red, and strontium and barium produce such striking effects that they are used for making red and green fire. The prism of the spectroscope refracts the different kinds of light emanating from any source at different angles, and thus disperses it, that is, spreads out the different constituents upon a screen, so that it may be examined in detail. Ordinary white light is a complex made up of the colors of the rainbow, usually said to be violet, indigo, blue, green, yellow, orange, and red, and when white light is examined in the spectroscope, all these colors are seen ranged in their proper order. The light from sodium, however, is pure yellow, and as seen in the instrument consists only of a narrow yellow band, no other colors being present. Potassium and lithium simi-

larly show bands in the red region, and cæsium and rubidium also have marked lines. The metals of the calcium group emit light which is somewhat complex, hence their spectra show several lines. Other elements also have spectra which are characteristic. They serve as clear methods of identification.

When sunlight is introduced into the spectroscope, it forms the regular multicolored spectrum due to the glowing mass of the sun. The gaseous elements on the surface of the sun also show their characteristic lines, but on account of the greater intensity of the light from the main body of the sun, these lines appear as shadows against the bright background of the rainbow colors. From these shadows, called the Fraunhofer lines, the various elements in the gaseous layers of the sun may be positively identified. The result from these studies and those of other heavenly bodies shows them to be composed of the same elements as the earth. In 1869 helium was thus discovered in the sun, and thirty years later it was discovered on the earth, also by the spectroscope.

OTHER PHYSICO-CHEMICAL PROPERTIES

The illustrations of the preceding pages of this chapter have been outlined somewhat fully, in order to give a definite and complete impression as to the nature of the physical studies useful to the chemist. In another place other physicochemical subjects were discussed in some detail. The gas laws, the ionic hypothesis, simple electrochemistry, the periodic classification, the phenomena of radioactivity are so intimately concerned in even an elementary study of chemistry that their discussion as a part of that subject is profitable, almost indispensable.

It is desirable to outline, in a brief way, even if somewhat disconnectedly, many of the remaining topics of physical chemistry, showing in a few words what meaning these have in interpreting our subject. Even the incomplete list of topics is a fairly long one, and their number is ever being increased. Grouping these topics from a physical standpoint is unsatisfactory, and it is not essential, as the chemist's interest is in the applications, not in the methods. For example, a number of very different methods are used which lead to knowledge of molecular weights. For the chemist they belong together, even if one concerns measurements of gas volumes and the other of the variation in freezing point or boiling point of a liquid.

VAPOR PRESSURE

The melting point of solids, and the boiling point of liquids, as has already been implied, are associated to a considerable extent with their chemical composition. The influence of substances in solution has also been discussed. Further considerations are still before us. When a liquid is heated, and begins to boil, the gas in expanding into vapor must overcome the pressure of the atmosphere. And as this pressure varies the boiling point varies. On a mountain 10,000 feet high the boiling point of water is only about 90° C., 194° F., while under pressure in a steam boiler the boiling point may be as high as 180° C., or 356° F. If the temperature of a liquid is raised indefinitely, there is reached a temperature at which the liquid is converted to a gas regardless of the pressure. This is called the critical temperature of the liquid. Before this fact was appreciated, it was found impossible to convert certain gases to liquids, because pressure alone was applied, and

above its critical temperature a substance cannot exist as a liquid. The name "permanent gases" formerly applied to oxygen, nitrogen, and other gases no longer has any meaning. These gases are now liquefied very readily by the combined action of high pressure and low temperature.

In the conversion of matter from one state into another, the change is often delayed after more than sufficient heat or cold has been applied. Vapors partially filling the space in which they are confined are common. When cooled they are not always condensed. They need nuclei to condense about, and since dust and smoke form such nuclei, fogs are prevalent over cities in moist regions. The rapid formation of clouds and gathering of rainstorms may be connected with this condition of supersaturation, which, due to its sudden cessation, causes great accumulations of liquid water. The reverse condition, overheating of a liquid without its boiling, is a source of constant annoyance to the chemist. The condition applies most often to concentrated solutions. When these overheated solutions do finally give off vapor, they do it with such violence that they may throw the liquid from its container. In a smaller way this sudden evolution of the gas causes the "bumping," which is at times extremely annoying. Liquids may be supercooled, and often such a supercooled liquid may be caused to solidify with great suddenness. Exact measurements show supercooling to be very common. An interesting application of this idea is the explanation of the peculiar properties of glass. Glass is such a complicated substance that its constituents do not crystallize out as it cools. This state of supercooling is never ended by a real solidification, namely, crystallization. The

supercooled liquid has no definite solidifying or melting point. It softens gradually on warming, and hardens gradually on cooling. The transparency of the liquid condition is maintained throughout. Thus two of the valuable characteristics of glass are due to the supercooled condition. The only change of state which shows no delayed action is the conversion of a solid into a liquid.

The boiling point of a liquid is the temperature at which its vapor pressure overcomes the atmospheric pressure. Vapor pressure is the tendency to pass into the gaseous form. A knowledge of the vapor pressure of water is needed in making gas measurements when these gases are in contact with water, for part of the space supposedly filled by the gas is taken up by water vapor. The vapor pressure of a liquid is altered by the presence of a substance in solution, the extent of the alteration being determined by the proportion of molecules present. From such studies the molecular weight may be found and so the chemical composition of a substance determined. The separation of the constituents of a mixture by means of their different vapor pressures is a very frequent practice in organic chemistry.

THE GAS LAWS

The gas laws are so intimately related to general chemistry that it seemed advisable to study them in that connection. We have done so, and need here to outline them only briefly. The kinetic theory of gases assumes the free motion of molecules through distances very large in proportion to the size of molecules themselves, although very small in comparison with distances with which we are familiar. In rough measurements the space through which the

molecules move is alone considered, and the space actually taken up by the molecules themselves is neglected. The attraction which molecules have for one another is also left out of account. When gases are highly compressed, however, these two factors count, because the spaces between the molecules are no longer so large by comparison and the molecules being crowded closer together assert an attraction which was before inconspicuous. By the appreciation of these deviations from the gas laws we obtain a more exact understanding of the nature of the molecule. By the comparison of gases we have a very satisfactory means of determining the physical nature of molecules. Chemical investigation tells us the nature and the relative number of atoms in a molecule, and how the atoms are linked together, but we need the help of physical means to determine what the absolute size of the molecule is. CH_2O and $C_3H_6O_3$, are distinguishable as soon as we convert them to gases and determine the molecular weights. The size of molecules and the speed and extent of their motion are determined by distinctly physical measurements. The understanding of these physical characteristics of molecules aids greatly to our appreciation of their chemical composition.

ATOMIC WEIGHT

The atomic weight is more nearly a chemical function than most of the other topics discussed in physical chemistry. Yet the determination of masses (weighing) is physical, the knowledge of the molecule so closely related to the atom is physical, and there are various other considerations of similar nature coming into play. The determination of the atomic weights is a delicate and intricate affair

and requires a combination of physical and chemical processes differing greatly for the various elements. The periodic classification of the elements is usually considered a chapter of physical chemistry. The atomic volume curve (a different expression and confirmation of the periodic law) is based directly upon atomic volume, which in turn is determined by dividing the atomic weight of an element by its specific gravity. Here again an intimate relation is established between a physical property, specific gravity, and the general chemical nature of the elements.

ATOMIC STRUCTURE

The structure of the atom is a topic which is of the foremost importance to the chemist. There is chemical evidence of an indirect nature, the resemblances and differences between chlorine, bromine, and iodine, for example, to warn us of the complexity of the atom. But the clear understanding of the matter has come from the study of radioactivity with its attendant physical phenomena. The study of radiations and similar purely physical experience paved the way for the understanding of the radioactive elements. Radioactivity is manifested by heat development, light development, electrical effects and the chemical changes which are accomplished. These are mostly purely physical phenomena. From all these considerations we derive the knowledge of electrons and have obtained a more satisfactory conception of the atom than before. The study of subatomic phenomena has become an important branch of physical chemistry.

HEAT

Measurements involving heat are, next to those of mass, the most common physicochemical measure-

ments. Temperature changes indicate development of heat, often from chemical sources, a fact in which we are interested every moment. We must understand thermometry and appreciate the meaning of the absolute zero, and of absolute temperature, points already brought out.

When a chemical reaction of the more ordinary kind takes place, heat is evolved and may be measured by the calorimeter. At first thought it would seem that we have in the amount of heat evolved a valuable physical measure of chemical affinities. It is of great value, but most chemical reactions involve so many features that the exact meaning of many results is lost. When carbon burns, the heat developed involves not alone the result of the union of carbon and oxygen, it involves also the conversion of solid carbon to gaseous carbon dioxide, and perhaps chemical changes in the disintegration of the complex carbon molecule. Yet in many ways the determination of the heat of a chemical reaction is valuable, as for example in the study of the fuel value of foods. This leads simply enough to the relation of chemical energy to heat and other forms of energy.

Specific heat is the relative heat capacity of various substances compared with water. It takes only about one-eighth as long to heat up a pound of iron through a certain number of degrees as it does a pound of water, using the same heat supply. Hence the specific heat of iron is only one-eighth. Specific heat has been a valuable means of checking atomic weights, for the product of the atomic weights by the specific heats of the elements has been found to be uniformly about 6.3. Chemical analysis tells us that silver has a combining weight

of 107.88. This may mean an atomic weight of 107.88, or some multiple of that number. To determine which value is correct, we need only divide the specific heat of silver, 0.056, into the constant 6.3, and the result, 112, indicates that the atomic weight of silver must be 107.88.

Heat Absorption of Gases.—When a gas absorbs heat, this heat is used to increase the molecular activity of the gas and also to increase the motion within the molecule. When the heat absorption is such that the second effect is not noticed, it may be inferred that the gas is monatomic, that is, there is only one atom to the molecule, so that no heat would be absorbed by motion within the molecule. This applies to mercury vapor and also to gases of the helium-argon group.

OPTICAL PROPERTIES

The value of the spectroscope in the study of the nature of chemical substances has already been discussed. The application of the former of these to the X-ray spectra of the elements has led to the development of the atomic number. This has given promise of the solution of two especially interesting problems, the anomalies of the periodic system and the total number of the elements. The atomic number of uranium, 92, seems to set the limit to the possibilities of our discoveries.

The Polariscope.—This is a physical instrument which gives us a glimpse of the internal structure of the molecule. It is of value in the study of substances like tartaric acid, the sugars and the amino acids. These all contain one or more carbon atoms of the kind called asymmetric. This means that the four bonds of the carbon atom are attached to

four different groups, making possible different arrangements in space about this central carbon atom.

Index of Refraction.—Another optical observation is often made use of, namely, the index of refraction. Like specific gravity, melting point, boiling point, and crystalline form, this physical property may be of use as a means of identification, especially in connection with the fats.

THE SPEED OF REACTIONS

The speed and completeness of chemical reactions are determined to a considerable extent by certain physical conditions, temperature, concentration, solution, and the presence of a catalyzer. It is a very common experience that an elevation of temperature greatly accelerates the speed of reaction. In fact, some reactions seem to stand still, and for all practical purposes do stand still, at ordinary temperatures. When heat is applied, these reactions proceed rapidly. It is a convenient laboratory rule that an elevation of 10° C., 18° F., doubles the speed of reactions. It is natural to attribute this increased velocity to an increase in molecular and atomic motion, but it is evident that the rate of increase of the molecular motion is far exceeded by the increase of chemical activity.

Concentration.—If an active metal is contained in a test tube with some water, and a little sulphuric acid is added, we may look for a reaction between the two. If no action takes place, the natural impulse would be to add more of the active acid. We here illustrate in a simple way the law of mass action, that the speed of the reaction is proportional

to the reacting masses. In this illustration the concentration of the acid alone counts, as the extent of the metal surface exposed does not vary. If the concentration of both participants in the reaction can be varied, the speed of the reaction, other conditions remaining constant, will be represented by the product of the two concentrations, $a \times b$.

Catalyzers are often mentioned and they are of the greatest use in accelerating the speed of reactions. At the present stage of our knowledge we are unable to formulate a complete explanation of their action. Some of the possibilities have already been explained.

SOLUTION AND ELECTROLYSIS

The condition of solution is intimately associated with chemical reactivity. So important are the various features of solution that they have been described in the general chemistry. In this brief discussion there is little to be added. The interesting feature of solution is that the molecules are reasonably free to move and show certain properties akin to those of gases. They exert a pressure, called osmotic pressure, which drives the molecules out into the solution, and the laws of osmotic pressure are very similar to the gas laws. As in the case of gases, the effects are determined not by the absolute mass of the substance present, but by the proportion of molecules. The influence on the boiling and freezing point of liquids by a substance in solution is another phase of this question. The abnormal results obtained for acids, bases, and salts dissolved in water, and the interesting conclusions derived therefrom, complete the sum-

mary of individual points touched on under the head of solutions.

ELECTROCHEMISTRY

The simplest elements of this subject have been outlined. The whole is very extensive, and in ways both theoretical and practical would carry us very far. This branch of physical chemistry has become so important that it has grown to be a subject for itself, and by the side of other branches commands its own textbooks and journals. We need not discuss it further.

COLORS OF COMPOUNDS

Color in compounds, both inorganic and organic, is the exception. Among inorganic compounds we usually associate color with certain metals. This is not by any means irregular, as colored compounds are associated mostly with metals in groups of approximately equal atomic weights. Among organic compounds color and dyeing properties are associated, as is shown in another place, with a very definite type of molecular structure. Such relations are very frequent subjects for physicochemical studies.

CRYSTALLINE FORM

Crystals are studied by mathematical and optical measurement, but that which gives them their crystalline form must be the chemical composition of the substance. For this reason chemically similar substances often crystallize in similar crystal forms. The crystals of chlorides, bromides, and iodides of sodium and potassium are all very much alike, for these salts are chemically similar. The alums form an interesting group of substances. Their formula may be written thus: $M^{I}M^{III}(SO_4)_2,12H_2O$. They

are double sulphates, containing always a metal of the sodium group and one of the aluminium group, crystallizing with twelve molecules of water. The crystalline form of all of them is so similar that a crystal of one placed in a solution of the other continues to grow, although one may contain the metals potassium and chromium, and the other ammonium and aluminium. This relationship is called isomorphism and was of some value for establishing the relationship of elements before certain better methods were established. In the case of these alums, for example, the metals which go to form them must belong to the M^{I}, the sodium group, or to the M^{III}, the aluminium group. The internal structure of crystals has recently been submitted to investigation by the so-called X-ray analysis. Such new studies, besides opening up new lines of thought, often serve to establish more firmly assumptions previously held.

SPECIFIC GRAVITY

The specific gravity of pure substances is of value as a means of identification. This applies particularly to minerals. It is connected to some extent with chemical nature. Metals of the sodium and calcium group are light, while the rest, excepting aluminium, are distinctly heavier. Metals with high atomic weights have high specific gravities, a fact true also of their compounds. There are exceptions to this statement, but as a rough generalization it is correct. Aside from any relation to the nature of elements and compounds, the specific gravity of solutions is used with great frequency for determining the proportions of the constituents. In the books containing the physical constants of chemical substances the tables covering this matter fill many pages.

COLLOIDAL CHEMISTRY

Between the condition of true solution, in which the molecules are diffused through a liquid, and a condition like that of coarse particles of sand in water, there are many phases of an intermediate condition, called the colloidal condition. This has been described as small aggregates of one substance more or less permanently surrounded by films or layers of another. Illustrations will make this clearer. A dust cloud represents fine particles of a solid in a gas, the air. Foam represents such a relation between a liquid and a gas, although we may produce a foam with a solid. The colloidal conditions most considered, however, involve suspensions of fine particles of solids, as of the metals, in water, emulsions of oils in water, and finally the hydrosols and hydrogels represented by a gelatine solution before it has set and after. None of these are true solutions. They consist of small particles of the substance surrounded by films of water. The different forms which these associations of particles and surrounding water take on run into each other, and sharp classifications may not be made.

The colloidal condition applies to small particles of substances mechanically divided, or to molecules or molecular aggregates so large that they do not form true solutions. The realm of the colloidal particles may be set as between the particles which are more or less apparent, and capable of settling out, and those of true molecular dimensions. These fine particles are kept from aggregation for a number of causes. The Brownian movement is a movement among particles small enough to be affected by the blows of the ever-moving molecules, and hence they are in a small way kept stirred up. Further,

colloidal particles are charged electrically with charges of a similar nature, hence they cannot collect, as particles with similar charges repel one another. When this mutual repulsion is the cause of suspension, the colloidal condition is brought to an end by the introduction of an electrolyte, when the particles lose their charges and can collect and settle. Another cause for the colloidal condition is the formation of films, which are persistent and prevent the particles from coming together. Such films around the fat globules of milk are familiar.

The colloidal condition has certain characteristics by which it may be recognized. The particles are visible by the ultramicroscope. The particles themselves are not actually observed, but only the reflections of a strong beam of light sent through the solution. The Tyndall effect is comparable. It is the visible path of a beam of light sent through a colloidal solution. Such solutions are opalescent, that is, not quite clear, and are likely to be viscous and easily shaken into a froth. Coagulation, most familiar in the hardening of egg white and the curdling of milk, is an interesting characteristic of colloids. Besides this form of gelatinization, we know also the setting of jellies upon cooling, or on account of loss of water or for other causes. Colloidal metals and other substances can be made to precipitate, especially by the addition of an electrolyte. Some forms of coagulation are simply comprehended thus: in the solid or liquid state, the solid is surrounded by the liquid and the liquid phase predominates: in the coagulated mass, the conditions are reversed and the solid form predominates.

The applications of colloidal chemistry are many, and when the subject is more fully understood we

will find therein explanations of many phenomena now simply passed over in wonder. The following list of applications indicates the large possibilities which may open up upon the better understanding of this absorbing subject. The chemistry of soap and of cleansing, leading on to the question of emulsions connected with the fats and greases, lubricants, and salves; the question of milk and milk products; paints with their suspended pigments; varnishes; inks; adhesives, starch, gums, and glue.* Gelatine and its use in foods; rubber, collodion, celluloid, products like imitation rubber, called plastics; photographic emulsions and negatives; artificial textiles, tanning; clay and the ceramic industries, including coloring and enamels; the application of dyes; the purification of water and the disposal of sewage; certain methods, as flotation, in metallurgy. Many of the problems of biochemistry are likely to find their solution in the field of colloidal chemistry.

It may be difficult at first sight to see the connection of all these substances with each other. The connection lies in the intimate and somewhat permanent association, which is not solution nor yet mere mechanical mixture, between different constituents. The final products are comprehended under such ideas as viscous solutions, as water-glass, varnishes, and glue; jellies, gelatinous solids, as rubber, celluloid or coagulated masses; pastes, as clay; emulsions, as milk, paint and photographic plates. Adsorption and contact catalysis are phenomena whose association with the others is not apparent, but their problems are nevertheless the same.

* The Greek word for glue, collos, has given its name to the subject.

CHAPTER XXVII

SANITARY CHEMISTRY

THE recent years have been measured by great progress in the work of sanitation and public health. In this valuable work chemistry has played some part, and what that part is will be here reviewed. The chief lines of its usefulness have been in the investigation of water supplies and the purification of these, of the disposal of the two great wastes, sewage and garbage, in the discussion of the vitiation of air and the problem of ventilation, and in the preparation of disinfectants, antiseptics, and of various drugs.

WATER SUPPLIES AND PURIFICATION

Only a limited portion of our population is privileged to use as a water supply a source which has incurred no danger of pollution. The limited population is that of sparsely settled regions, especially in mountain districts, and a few favored municipalities which are so near unsettled regions that they may draw upon them for their water. In another class are cities like New York and Boston, which by the proper precautions keep their watersheds free from danger even in regions adjacent to settled communities. In this class, though the source is very different, come those homes and communities which use ground waters from wells, which are safe because they yield unpolluted waters, or waters whose

slight pollution has been cleared up by their long passage through the layers of the ground. The great danger in water supplies lies in the fact that many large communities are dependent upon surface water supplies, rivers, or lakes, which have been polluted either by themselves or by others. No better example can be cited than that of the Ohio River, which serves alternately for the water supply and the sewage receptacle of Pittsburgh, Cincinnati, and Louisville. Surface waters require the most consideration because they are so much used, and at the same time are the most polluted.

Water is likely to take up substances of two classes, the inorganic or mineral, and the organic. The soluble inorganic constituents are mostly the salts of calcium and magnesium, which make the water hard. There is no evidence that they are ordinarily prejudicial to health. Other inorganic substances, like common salt, are unimportant in all but most unusual waters.

The organic constituents, especially the bacteria, are more important. We could perhaps tolerate, upon suppression of our purely esthetic sentiments, the waste products of men or animals, if it were merely dead material. But when these waste products include disease-bearing bacteria, the pollution ceases to be a matter of taste. Cholera, typhoid, and intestinal troubles like dysentery are the specific troubles to be feared, while the general tone of health of a community is said to be generally benefitted when the water supply is improved. Of these diseases typhoid fever is the most serious menace, and as it is so clear that it is in great part preventable, the pathos of it is the greater. Typhoid fever is not to be feared on account of a general condition of

water supply. The danger is due to specific contamination by the excreta of typhoid sufferers. Any water contaminated by sewage is likely to be infected.

It will not be advantageous to tell about the methods of chemical analysis of water supplies. This analysis tells much about the history of the water and its possible pollution, but the particular condition of bacterial pollution is to be found by bacteriological methods. The chemist is then called upon to help the engineer to devise means of purifying water which is contaminated or which may be in danger of becoming so.

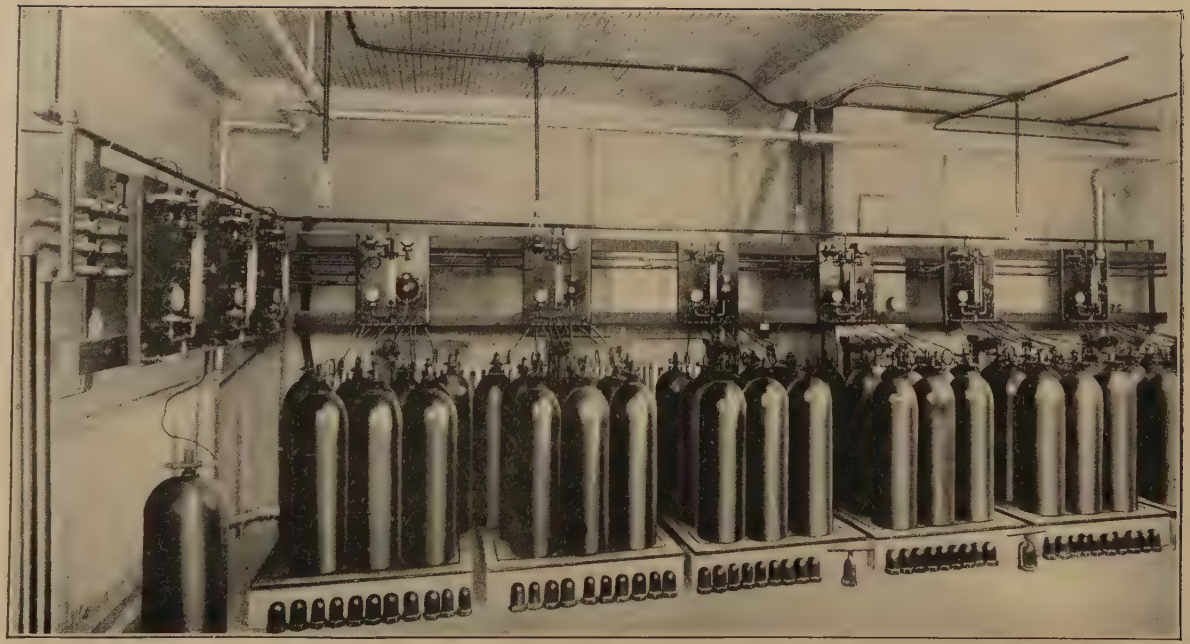
There have been various methods suggested in the past for making water safe. On the large scale reliance is now placed almost altogether on filtration and chlorination. Filtration is by the rapid or slow sand filter; each has its advantages, but the rapid filters are gaining ground rapidly in America.

Slow sand filtration, suggested by the process of natural purification as water passes through the ground, consists in passing the water downward through a layer of sand about three feet thick. There is soon formed a sediment layer on top of the sand (German, Schmutzdecke) which is a very efficient filtering medium. Any sediment or bacterial matter is retained by this layer, and the effluent is a safe one. In the course of time the layer becomes so thick that it must be removed. The water is then drawn off and the sediment layer scraped off. This is a cumbersome, expensive, and even unsanitary necessity and counts against the process, although mechanical improvements have diminished the objections. More serious are the objections that the filter beds require large areas, and in cold climates must be covered to prevent freezing. Yet London

and other large cities use this method with success. In America the waters needing filtration are likely to be turbid, and this turbidity hastens the clogging of the filters and diminishes their efficiency. But the quality of the water supplied in the cities using them has been good.

The rapid sand filters are more popular in America. The essential differences are these: The necessary filtering area is cut down to about one-fiftieth, by the use of a larger-grained sand. To accomplish the filtration with the coarser sand, a coagulant is introduced which serves to entangle the matter to be removed and to form a filtering layer on the sand. The third essential feature is that through mechanical contrivances the flow of water may be reversed at a high rate of speed, the accumulated deposit washed from the sand layer and thus the filter renewed. This renovation is a matter of a few minutes, and the combination of mechanical manipulation and prompt restoration to use is a very important item. The process of the operation is this: As the water enters the system the coagulant is added. This is either alum (aluminium sulphate) or ferrous sulphate and lime, which are converted respectively into aluminium or ferric hydroxide, substances of gelatinous nature. The water is thoroughly mixed with the coagulant, then allowed to flow slowly through settling chambers for several hours. During this time the greater portion of the coagulum separates out, and the rest is removed on the filters. All insoluble matter including sediment and bacteria are thus completely entangled and removed. When properly operated, especially in respect to crowding, the rapid sand filters yield a safe and attractive product.

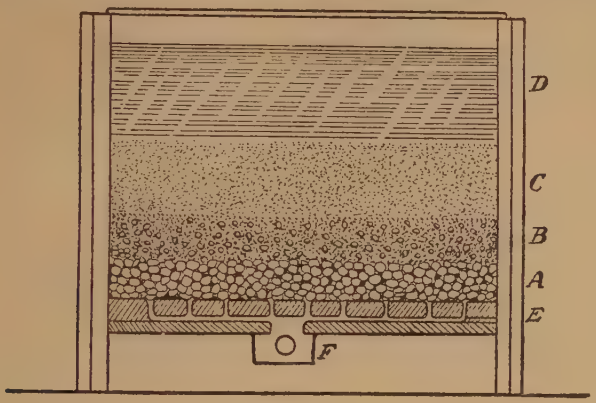
SPRINKLING FILTERS NEAR BERLIN



Courtesy Scientific American

CHLORINATION PLANT FOR PURIFYING NEW YORK CITY WATER

Chlorine has been spoken of as a bleacher and disinfectant. In recent years it has been applied to the disinfection of water supplies with marked success. It cannot take the place of filtration with some waters, for example, turbid waters. Any highly polluted water should be filtered. But as an aid to filtration, for the treatment of waters which are



A FILTER UNIT

A, represents 12 inches of small stones, ¾—1½ in. B, graded smaller stones and coarse sand. C, about 2 feet of standard sand, which serves as the filter. The water stands 3 feet above the sand. The collecting drains E, lead to the main drain F.

almost good enough, and as an emergency measure, chlorine is a great boon and has already saved many lives. The expression "chlorine" is used, although it is applied as the element in the form of liquid chlorine or in compounds in the form of calcium or sodium hypochlorite, all possessing equal efficiency.

The typhoid death rate is a gruesome but convenient method of determining the safety of a community's water supply. This is the yearly number

of deaths per hundred thousand of the population. Roughly speaking, one death represents ten cases of sickness from the disease. The following tables show very clearly the relation of pure water to the typhoid death rate.

Table I shows the improvement which has been accomplished through a period of years by improvements in water supplies and other means of sanitation. It represents the annual typhoid death rate for thirty-six northern cities of the United States of over 100,000 population through a period of years.

TABLE I

1890	1900-1905	1906-1910	1911-1912	1918 (20 cities)
58	31.5	24.5	13.3	5.4

Table II shows the rates of a number of cities for several years immediately before and after the introduction of a new water supply.

TABLE II

Cleveland, 1900-'03, annual typhoid rate...	57	After the new supply, 1905-'10	15.8
Cincinnati, 1906, annual typhoid rate....	71	After the new supply, 1908-'12	11.2
Pittsburgh, 1906-'07, annual typhoid rate...	138	After the new supply, 1909-'12	10.3

The hardness of water is caused by compounds of calcium and magnesium of two different types. The first type includes the acid carbonates, $H_2Ca(CO_3)_2$ and $H_2Mg(CO_3)_2$. These are considered apart because, upon sufficient boiling, they are decomposed and the calcium and magnesium carbonates deposited and removed from solution. They are called temporary hardness, and the treatment is different from that for permanent hardness, which is due to

chlorides and sulphates of the same metals. The objections to hard water are two. Soap is destroyed by these compounds, and there results not alone the waste of soap, but also the formation of the well-known scum of the calcium and magnesium stearates or salts of the fatty acids. This substance adheres to utensils used with soap and remains to a certain extent in clothes washed in hard water. The other detriment in the use of hard water is the sediment of scale which settles out in boilers. This is absolutely serious, and must receive attention by all using hard water. In certain limited fields of manufacturing hard water is undesirable.

The chemical problem of softening is a simple one up to a certain point. We must convert the soluble calcium and magnesium salts into insoluble compounds, which may be allowed to settle out or are filtered off. The first class of compounds mentioned above is thus treated; $H_2Ca(CO_3)_2 + Ca(OH)_2$ lime, $\rightarrow 2CaCO_3$, insoluble and therefore harmless, $+ 2H_2O$. The reaction for magnesium is not quite so simple, but for our present purpose may be assumed to be the same. This assumption that magnesium reacts like calcium will be maintained throughout the discussion.

The softening of a city's water supply increases the attractiveness of the water. So far as the taste of hard water goes, habit differs, and the matter is not serious. But the other considerations are real. It is difficult to reduce the saving of soap and boilers to figures, but it is likely that any expense involved in the softening of water will be returned in the saving of soap and in boiler operation.

A method of water softening adaptable on a scale short of a public water supply has become somewhat

common. This is the treatment of the water with natural or artificial zeolites, double silicates of sodium and aluminium. When the water comes in contact with this substance, all the calcium and the magnesium from the hard water go into the compound, and thus become insoluble. The softening operation is perfect, for the sodium liberated in the place of the calcium and magnesium has no hardness effect. The softening agent must be restored occasionally by treatment with sodium chloride, common salt, when the accumulated calcium and magnesium are thrown out and the desired sodium restored.

SEWAGE DISPOSAL

Sewage normally consists of the city water supply, which has gathered up in its course through the city the various wastes which can be carried away by water. There is likely to be an increase in the mass of the sewage from the ground water, which seeps into the sewers, and in warm weather the loss from evaporation and use on lawns and gardens may cause a definite diminution. Storm waters, when delivered into the common sewers, complicate the problem of sewage disposal. Some communities have separate sewage systems. Until the dilution due to storm waters reaches the ratio of 3 to 1, the sewage is called sanitary sewage, and requires attention. With greater dilution the necessity of treatment for purification is diminished. In addition to human excreta, kitchen wastes, stable wastes, waste from soap and washings, industrial wastes and street washings must be reckoned with. Sewage may be considered 1,000 parts water and 1 part solid matter, of which ¾ is in solution. In America there is a much larger consumption of water per capita than in

Europe, and this increases the difficulty of the problem, which depends on the mass of water to be treated rather than concentration of impurities.

From the most superficial standpoint the treatment of sewage has for its aim the prevention of any nuisance. This includes unsightly refuse, odors, danger to bathers and to fish life, and finally pollution of any water used subsequently as a source of supply. The simplest disposal is running the sewage into large rivers or into tidal water under such conditions that no signs of the refuse are ever again apparent. This applies, or seems to apply, in many cases. The sewage of Buffalo once in the Niagara River will not trouble Buffalo again, and a city like St. Louis, or some of the cities on large swift European streams, are not again troubled with their sewage, when it is once discharged into the stream. Whether communities farther down stream notice the pollution is considered more or less a separate question. The same idea applied to lake cities or to cities on tidal harbors has not been so successful, for the flow of the water away is often not sufficiently pronounced. In the Great Lakes and in New York harbor the accumulation of pollution is a problem.

In the last analysis, sewage treatment has for its ultimate object the completion of the nitrogen and carbon cycles already mentioned in another connection, so that the material which has become waste by human use may be so altered that it is unobjectionable, safe, and ready to be taken up for plant growth. The various bacterial methods of treatment have for their immediate practical object the alteration of waste matter, in such a way that it is moved along in this cycle. It must thus reach a point, so that in

the ordinary course of events the process may be completed by nature without any further attention or objectionable features.

Although there are many other features connected with sewage which interest the engineer, the greatest menace to health lies in disease germs present. If these are destroyed, one great problem of sewage disposal is solved, but not all. When sewage is so treated that the nitrogen cycle is completed, and oxidation fully carried out, dangerous bacteria are destroyed. It is therefore only occasionally true that sewage must be treated specifically for bacteria. It is usually treated in a general way and the refinements of bacterial safety left to the finishing touches of water purification when the water is to be used again. It is evident that the making of sewage more pure than the water into which it is to be discharged is an overrefinement.

Running sewage into large bodies of water so that it seems to be removed from our attention, means dilution with so much water charged with oxygen that the operation of oxidation may take place promptly and completely. The Illinois river presents an interesting study. The sewage of Chicago, discharged into this stream, is too great a burden for it to take. Consequently the river is a polluted river, containing no dissolved oxygen and no fish life for many miles. In course of time the absorption of the oxygen from the air rectifies this condition, and the river becomes normal, so that it is not considered a menace to the water supply of St. Louis, farther down stream. Boston meets this problem of sewage dilution by storing its sewage on an island, well out in the bay, for periodic discharge into the sea at ebb tide.

The soil has striking powers in oxidation of waste, and conversion of offensive matter into the innocuous constituents of the soil. In the use of barnyard manures and the disposal of household wastes in the country we see constant application of this. But as soon as people concentrate, the accumulation of refuse is too great for this kind of disposal and the problems of sewage disposal develop. Carrying the sewage out to the country, and applying it to the land is then only logical, and where the winter is open enough, it is not uncommon. Berlin, Paris, and many small English cities use the method of irrigation, which means applying to the soil as much sewage as the soil can dispose of, using the land at the same time for the growing of crops. The land is underdrained, and the process, given favorable climatic and soil conditions, is satisfactory, and the cost is not excessive. The amount of land needed is very large. There are modifications of this method, wherein the growing of crops is left out, and the soil used more in the sense of a filter.

London uses a method of chemical treatment. After screening and some sedimentation, the sewage is treated with ferrous sulphate and lime. The precipitated iron hydroxide carries down with it a considerable fraction of the material, not soluble, and the whole is allowed to settle. This sludge, which is still 95 per cent water, is carried out to sea by steamers, and scattered over so great an area of open water that no signs of it are again apparent.

On the whole chemical treatment is not so promising as bacteriological treatment, which is the natural way of disposal. Disinfection, for example, is only of value in specific cases, as for destroying

the disease germs when there are sewage outfalls near bathing beaches. On the whole it delays too much the bacterial changes which are the ideal ones.

It can hardly be said yet that the methods of sewage disposal have been standardized. At present the methods of most promise are those depending upon bacterial action, either in tanks without air, or under the influence of air by means of beds or sprinklers, or even by forced aëration.

SEPTIC AND IMHOFF TANKS

In these the sewage flows so slowly that it is practically in a state of rest. Fermentation takes place, much of the material changes to gas and to soluble substances, and the effluent is in better condition either for running away or for further treatment. There is no sufficiency of oxygen, and the fermentation must depend upon bacteria of the anaërobic, that is, working without oxygen, order. For small installations this is sometimes all the treatment that sewage receives. The Imhoff tank has mechanical modifications which make action more perfect. A further treatment often applied is the exposure of this effluent to the air, sometimes by sprinkling it as a spray over the surface of broken stone which is covered with the residue of previous contacts. There is abundance of bacterial and insect life on these surfaces and the oxidizing and purifying action is considerable. This double treatment yields an effluent which under ordinary conditions is considered satisfactory.

The activated sludge treatment makes use from the beginning of bacterial action favored by an

abundance of oxygen. These bacteria are developed by blowing air through a portion of the sewage, until it is apparent that they are present in abundance. After this the incoming sewage is treated with the sediment of previously treated sewage, all the time being exposed to a vigorous circulation of air. The mass becomes brown, and upon standing the solid matter settles out so completely that the effluent is of satisfactory appearance and "stability," that is, will not putrify. The activated sludge method is compact, quick, and satisfactory in many respects. But as yet two features are drawbacks. The blowing of the air is wasteful and expensive. And the sludge from the settling tank is still to be disposed of. It promises to have a high fertilizer value, but as obtained contains so much water that it must be dehydrated in order to be applicable. This problem has not yet been solved from the standpoint of economy.

In this question of sewage purification it must be appreciated that the chemical side of the question is only one. The engineering question is a very large one, and the whole operation must be carried out so economically that it shall not be an overserious burden to the community. The fertilizer value of the sludge from the various treatments will probably not be more than enough to cover the expense of handling. The increasing population of our cities and the higher sanitary ideals demand a solution of the problem. If it cannot be solved at low expense, we must be prepared to submit to a greater expense. The pollution of our river, lake, and harbor banks, to say nothing of our water supplies, will be tolerated less and less as time passes.

GARBAGE DISPOSAL

The average city dweller, certainly until the war opened up new ideas on the value of foods, looked upon garbage as an offensive nuisance, to be gotten rid of in any way possible. This is wrong. Garbage is simply the product of agriculture, which, having been brought into the house, is not available for any use in that home. It is not necessarily a nuisance, and its destruction is a form of waste. The garbage of New York City, after it is collected and delivered, is worth a million dollars a year. Attention may be called again to the nitrogen cycle. The much-talked-of nitrogen question concerns the placing of the nitrogen of the air, that is, uncombined nitrogen, into combination, thus making it part of the nitrogen cycle. Burning garbage converts the combined, that is, usable nitrogen, into uncombined, that is, useless nitrogen, which is now out of the cycle. Burning of garbage is then to be condemned, especially as so many methods are offered for its proper handling.

Garbage disposal takes two forms, mechanical treatment and feeding to hogs. In the former case details differ, but the outcome is that the fat present in garbage is extracted by a proper solvent, and the dried residue is used as a constituent of artificial fertilizers. The other method, feeding to hogs, is receiving increasing attention. Farms where this is accomplished must be conducted in a most thorough manner, to prevent nuisance and disease, but these establishments have not the offensive features which popular ideas associate with them. In this method, as the other, the purpose is to utilize, not to destroy, that part of the food which has not been disposed of.

VITIATION OF AIR AND VENTILATION

It is evident that the air in confined spaces soon loses its attractiveness when it is breathed or otherwise used. Unless the circumstances are extreme, it can be shown that the harmfulness of such air is not due to an appreciable loss of oxygen, nor is it due to an accumulation of carbon dioxide, for air, otherwise fresh, when mixed with carbon dioxide from chemical sources still retains its freshness. Within a few years a New York State committee on ventilation made a study of this subject, and although their results in some respects were indecisive, several points were well established. These were: The increase of carbon dioxide has no effect on the quality of the air; there was no sign of any poisonous substance in the air of ill-ventilated rooms; the amount of moisture in the air was an important factor, as was also the temperature of the air and its condition of rest or motion. These last features are associated with the heat-regulating power of the body and in this factor the final solution of the effect of bad air will probably be found.

Ideal ventilation would require that there should be a flow of air through a given room, so that at every moment its occupants would receive an absolutely fresh supply. Such a condition, when the air must be warmed, is excessive in cost, and in its place a practical program is adopted. This provides for addition of fresh air to dilute the vitiated air until it is sufficiently healthy and comfortable. Three thousand cubic feet of fresh air per person per hour has been an adopted standard. This is about 1/10 of the amount flowing over a person in the open on a quiet day. There is always considerable passage

of air by leakage through crevices or diffusion through the walls. An official standard set by Chicago is as follows: 1,800 cubic feet per person per hour, velocity 2.5 feet per second, carbon dioxide 8 parts in 10,000 (that is 2 to 3 times normal), temperature 20° C., 68° F., humidity 42 per cent, dust count 100,000 per c.c.; bacteria, 12 colonies per plate.

Vitiation of air by products of combustion, as in illumination and warming, from sewer gases, from industrial operations, as in chemical factories, are problems requiring special attention. Some startling results have been published recently showing the dangerous condition of the air in auditoriums during epidemics of colds.

DISINFECTANTS AND ANTISEPTICS

A disinfectant is a substance which is capable of destroying bacteria. An antiseptic is milder in its action, perhaps not destroying the bacteria which may be present, but rendering the medium unfavorable for further growth. There can hardly be any distinction between the two except that of degree, and the same substances act as both. Copper sulphate solution of 0.1 per cent concentration acts as an antiseptic, but of 1 per cent concentration it acts as disinfectant. Certain physical agents, as light and heat, destroy bacteria, but we are concerned here with chemical action. It is often difficult to explain how the chemical reagent acts. The following generalizations are in part somewhat vague, but they are, nevertheless, suggestive. Disinfectants destroy by acid action, by coagulation or precipitation of the bacteria or their food (the heavy metals readily coagulate most forms of protein); by direct poisonous action; by reduction and oxidation. In

some cases the action seems nothing more definite than the development of an uncongenial surrounding. Just as higher animals and plants can thrive only within circumscribed conditions it is likely that bacteria are hardy within only narrow limits.

Among the nonmetallic substances the active elements and compounds are naturally in the foreground. Chlorine, bromine, and iodine are very efficient, as are also compounds like chloride of lime which yield chlorine. The acids are efficient, but they are of limited application. Sulphur dioxide is much used, and calcium pentasulphide, lime sulphur solution, is an effective fungicide, although the manner of its action is not clear. Boric acid and borax have marked preserving action, although they are very mild chemical reagents. (Preserving action is akin to antiseptic action.) The heavy metals, particularly mercury in the form of mercuric chloride, are efficacious. After mercury, zinc and copper are the most used. Oxidizing agents like potassium permanganate and hydrogen peroxide are much applied.

Many organic compounds are valuable disinfectants. Their chemical reactivity is low, yet they are very inimical to bacteria. Foremost are the phenols, hydroxyl derivatives of the benzene series, carbolic acid C_6H_5OH, cresylic acid C_7H_7OH, and thymol $C_{10}H_{13}OH$. These are the important constituents of tar and creosote. Formaldehyde possibly reacts chemically with portions of the bacteria. A number of other organic substances are used for bactericidal purposes, but their enumeration would introduce no new ideas. In the present state of our knowledge the efficiency of any organic substance must be determined by direct bacteriological experiments.

CHAPTER XXVIII

AGRICULTURAL CHEMISTRY

IN the economy of nature, the processes of vegetable life are preliminary to those of animal existence. To some extent modern men utilize the stores of past ages, petroleum and coal, or rely on the energy of the sun as manifested in the power of falling water and the winds. Aside from these instances men are dependent for their existence and activities upon the food and the energy stored up for them by the growing of plants. Men and other animals must rely absolutely upon the vegetable kingdom for their sustenance, and, after using their food, return the spent matter to the atmosphere and to the soil to be applied again to the upbuilding of vegetable matter. Thus these two kingdoms of nature supplement each other. The carbon, hydrogen, oxygen, and nitrogen compounds pass through cycles, mineral to vegetable, to animal and back to mineral, the process being repeated indefinitely. Such a cycle does not, however, exist in regard to the energy development. The energy of plants, after being passed on to animals, is permanently dissipated by the latter, and the plants must draw a new supply from the sun.

It will be well to review the carbon and nitrogen cycles already mentioned in other places. From carbon dioxide and water plants build up carbohydrates, fats, and proteins; animals use these as food and burn them up to form carbon dioxide and

water. The cycle is complete, and the process is repeated. Nitrogen, too, goes through a cycle. Plant protein containing nitrogen is built up, serves animals as food, their waste is returned to the soil and thus is returned to the plants. We could imagine plants and animals mutually supplying each other, and establishing a continuous exchange of material without renewals from without.

The building up of the carbohydrates from carbon dioxide and water is the simplest of the plant syntheses. Carbon dioxide with water forms carbonic acid, H_2CO_3. Under the influence of the sunlight, aided by chlorophyll, the green matter of the leaves, a reducing action takes place and formaldehyde is formed, with the loss of two atoms of oxygen, which pass into the air. $H_2CO_3 \rightarrow H_2CO + O_2$. In this reaction as much energy is stored up as would be liberated if the reverse action should take place. This then is the source virtually of the energy by which the animal kingdom lives.

The formaldehyde, which for purposes of comparison may now be designated as CH_2O, polymerizes to glucose, or a similar substance, $6CH_2O$, or $C_6H_{12}O_6$, and from this unit all the carbohydrates are built up, including all the disaccharides like cane sugar, $C_{12}H_{22}O_{11}$, and starch and cellulose, $(C_6H_{10}O_5)n$, by the loss of water.

The fats in turn are derived simply enough from the carbohydrates. This is illustrated from the fact that starchy foods are fattening. In this transformation much oxygen is lost, so that the fats formed have a much higher food value than the original carbohydrates. The following equation:

$$9\tfrac{1}{2}\ C_6H_{12}O_6 \rightarrow C_3H_5\ (C_{18}H_{35}O_2)_3 + 2H_2O + 49O$$

Glucose — a typical fat.

is not designed to indicate any exact mechanism. But it does show that the change involves a large loss of oxygen which is used up by other molecules, and the resulting fat has therefore stored up much more energy than was represented by the carbohydrate from which it was derived.

The proteins are composed of units not dissimilar to those of fats and carbohydrates, linked together by means of nitrogen. It would seem unwise to try to explain their formation from carbohydrates when the matter is far from clear. However, no reactions essentially different from those already shown are involved. Even though the synthesis must involve nitrogen, the amino acid, $C_6H_{11}O_2NH_2$, a protein unit, might readily enough be derived from $C_6H_{12}O_6$, the carbohydrate, and ammonia, NH_3. All these syntheses involve absorption of energy, but that phase presents no difficulties, for absorbing energy from the sunlight is a prime function of plants.

Besides the three groups of compounds just discussed, vegetable organisms include a number of other simpler organic compounds, such as the organic acids, oxalic, citric, malic, and tartaric. There are other groups of substances as the essential oils of the spices, and the alkaloids of certain drugs. Their formation presents no new kind of problem, and we need not follow them any further in our discussion. To these four classes water and mineral matter must be added to make our list of plant constituents complete.

In the composition of plant and animal products the four elements, carbon, hydrogen, oxygen, and nitrogen are usually considered in a group by themselves, as they go to make up the great bulk of plants. Further, when these products are burned,

these four elements escape as gases, and all the others remain behind in the ash. These others are included in the name "mineral matter," and their presence is usually shown in the ash and their amount thus determined. The relation of mineral matter to the development of plants is even more obscure than in the case of the same relation in animals, but it is no doubt much along the same lines. The importance of mineral matter is apparent from the persistence of certain constituents in the ash of plants, and from the absolute necessity of these minerals in available form in any soil in which plants are to grow. As might be surmised, the minerals are compounds of the more common metals and nonmetals. The same five metals which are important among animals are found in plant organisms, namely, sodium, potassium, calcium, magnesium, and iron. Potassium is far more important than sodium. Among the nonmetals, phosphorus, sulphur, silicon, and chlorine are found.

What is the function of this mineral matter? It may be well to repeat in part some of the ideas of a similar discussion in the case of the chemistry of nutrition. Silicon dioxide serves to stiffen some stalks, as the wheat stalk. Phosphorus serves as a nucleus, like carbon, for the building up of complex molecules, as in certain proteins. The metals seem to form intermediate compounds, necessary to the upbuilding of vital substances. They may be influential in the chemical reactions taking place in the juices, and have some connection with the colloidal nature of the cell. They may have action like catalytic action.

Lastly, the rôle of water is of the greatest moment. It forms a large proportion of the mere bulk of the plant. It holds important constituents in

solution, serving as a storehouse and carrier for vital supplies, and as a medium for the process of chemical changes. It is a temperature regulator. It fills all the spaces of the plant, bringing about the rigidity of the leaves which is associated with the highest well-being of the plant. Water has chemical relations to growth, in the first place, as the source of the hydrogen of the plant, and, secondly, in the chemical changes similar to those in animals which take place in the plant, as the changes among the carbohydrates. The chemistry of the cell no doubt involves colloidal chemistry, and colloidal chemistry depends on water.

THE NATURE OF SOILS

Soil is not merely pulverized rock. It is rather rock reduced to fine form, through physical or chemical agencies, mixed with the soluble mineral matter which has been derived from the chemical disintegration of the rock, and with the organic residues from plants which have previously grown in it. The question of rock disintegration has already been discussed in the chapter on geochemistry. The summary of the ideas involved is as follows: Rocks, mostly silicates of a fair degree of complexity, are disintegrated, first physically, through temperature changes, glacial, water and wind action, even through the growth of plants. Upon the extensive surfaces thus exposed there is chemical action, due to water and carbon dioxide, oxygen, the juices of plants, and microorganisms. These chemical changes yield a limited amount of material of some solubility, which serves as the mineral plant food. Vegetation may now start in this mass, and upon the death and decay of the first plants growing, their remains are

added to the soil. If this goes far enough, our soil is complete; namely, a basis of inactive insoluble rock material carrying the available inorganic and organic plant food. It may be capable of yielding, by subsequent chemical changes, a new supply of soluble mineral food.

We may for convenience consider the inorganic, or mineral, constituents of the soil in three classes. The first class includes the constituents which are soluble in water and very dilute acids. The plant juices through their acid content are able to exert a more powerful solvent action than water alone. This class represents the most available plant food. The second class of substances includes those which go into solution in acid of greater concentration, about 20 per cent hydrochloric acid. This represents the plant food more remotely available. The third class includes the insoluble material locked up in the residue. It cannot support plant life until in the course of time its constituents are so altered that they belong to one of the other classes. In this connection the soils and vegetation on the slopes of Vesuvius are instructive. The solid lava beds gradually disintegrate physically, forming finely divided material, yet barren of vegetation. Near the base of the mountain, where the chemical disintegration of the lava has also taken place, in addition to the physical, vegetation flourishes.

Everyone is familiar with the fact that organic matter, such as dead leaves, roots, and barnyard manure, when mixed with the soil, presently loses its characteristic appearance and becomes merged in the soil as a part thereof. The expression, "good clean dirt," perhaps means that any trace of the origin of a substance, offensive or otherwise, has

been obliterated, and it is now all incorporated in the familiar soil. The conversion of ordinary organic matter into the normal organic soil humus involves two constituents, that part containing nitrogen, and that part free from nitrogen, in which the carbon is the center of interest. The nitrogen cycle again comes into consideration. The significant feature of this cycle is that nitrogen compounds, the proteins of decaying animal and vegetable matter, move along through a series of changes, involving a simplification of the molecules, until ammonia is reached, when oxidation begins to take place. In the end the nitrogen is fully converted into nitrates, which serve as the immediate supply of nitrogen for plants. These now rebuild the proteins, and the cycle is complete. The final changes of the cycle have not been completed when the nitrogen compounds are incorporated in the humus. These take place gradually as the nitrates are developed under the influence of bacteria. In the last form they are soluble and easily washed out of the soil and wasted. Hence their gradual formation is an advantage.

The changes by which ordinary carbonaceous organic matter becomes humus are difficult to follow. Some carbon oxidizes to carbon dioxide, but this is lost to the soil. As carbonaceous matter decays and ferments, it loses gaseous constituents, darkens in color, and is altered in texture. It is capable of absorbing and holding water. A soil rich in this humus is fertile, for humus from its origin is likely to contain in abundance the materials which plants require for their growth.

In the process of their growth, plants assimilate carbon, hydrogen, and oxygen from the carbon

dioxide of the air and the water of the soil. The other requirements, nitrogen and the minerals, are extracted from the organic and inorganic constituents of the soil. If the plant dies and decays where it has grown, much of that which was extracted is returned to the soil, and the amount of humus is actually increased. Agriculture, however, involves a heavy drain upon the soil when the crop is removed. Hence arises the necessity of the renewal of the available plant food from outside sources. The elements needed by plants for their growth are: sodium, potassium, magnesium, calcium, and iron among the metals, and silicon, chlorine, phosphorus, carbon, hydrogen, oxygen, and nitrogen among the nonmetals. Of these, carbon, hydrogen, and oxygen are supplied by the atmosphere and water. The rest must come from the soil. All but calcium, potassium, phosphorus, and nitrogen are so uniformly present in sufficient amounts that they seldom require any attention. These four, and especially the last three, may be wanting in a soil that has been cropped. One of the problems, therefore, of agricultural chemistry, is the study of the exhaustion and renewal of these forms of plant food. It has been claimed that most soils have enough mineral food stored up in the less available form to serve plants indefinitely, provided the soils are so handled that these foods become available. Whether this is true or not, it is very apparent that, in a short period of time, soils lose their fertility when crops are removed from them. The supply of easily available plant food is soon used up.

The process of fallowing is the simplest manner of renewing the available food. The land lies idle, but during this time the natural changes of rock

disintegration go on so that presently there is a new supply of the more soluble plant foods. This is a method now used only exceptionally. The same results are better attained by rotation of crops.

ROTATION OF CROPS

The different crops do not all withdraw the same constituents from the soil in equal amounts. One draws on the nitrogen heavily, another on the potassium, and a third on phosphorus, while in each case the other foods are in a measure spared. If, therefore, through a period of say five years, there is planted a succession of different crops, each will in its turn, while drawing upon its own specific requirement, allow the soil to recuperate with respect to the foods which other plants require. Rotation of crops is not solely a chemical problem. It must be managed with reference to other agricultural needs, such as the use of the seasons for planting, and a convenient distribution of labor.

To restore the plant food to the soil, to replace a sufficient fraction of that which has been taken away, or otherwise lost, is the purpose of fertilizing. Some soils are said to be capable of supplying the mineral needs indefinitely, but usually plant food must be restored, and the first method for accomplishing this is the use of barnyard manure. A detailed study of this topic is not in order here, but the main point is clear. What comes from the land thus goes back to it. To be sure, through the sale of products from the farm, there is some loss, but these products may be so selected that they bring a maximum of return with a minimum of drain. Dairy and poultry products illustrate this, for what they carry away is of smaller proportionate value than

the return they bring. If properly managed, the use of barnyard manure carries back to the land almost all that has come from it, so that the replenishing from outside sources may be reduced to a minimum. Akin to this fertilizer in theory is the use of such materials as tankage and other slaughterhouse products, the refuse of beets at the sugar extraction plants, garbage residue, and everything which has directly or indirectly come from the land. Of course, there is here a change of location, and one farm may be losing what another gains. Some such fertilizers have a specific value. Liquid manure is especially rich in nitrogen and phosphorus, bone meal supplies phosphorus, wood ashes yield potash. Barnyard manure and other fertilizers often have humus-forming value in addition to the specific enrichment, potash, phosphorus, or nitrogen, which they supply.

It may be well to mention the use of human sewage in this connection. The first difficulty in the use of this source of plant food is that the sewage problem is primarily one of sanitation and human convenience. In the solution of this problem, in the removal of human excreta so that they no longer endanger health or offend the senses, the refuse is frequently so diluted that its recovery will involve a greater outlay than the return will warrant. That question becomes a much mixed one. If in the course of time our natural resources are considerably diminished, the situation may be altered, and men may consider the effort worth while. This already applies in some oriental countries in ways which we may hope will never be ours. But the utilization of sewage sludge from the modern methods of sewage disposal is a topic receiving the

most serious attention. If the high fertilizer value of the activated sludge residues can be practically realized, the return from this source may make this method, so satisfactory in chemical respects, satisfactory also from the economical standpoint.

In the use of artificial or commercial fertilizers, the special chemical nature of the problem becomes conspicuous. Some commercial fertilizers do not suggest any new points over what has already been discussed. Tankage and garbage residues are simply other phases of the theme mentioned under barnyard manure. But in the use of the various nitrogen compounds, phosphate rock, and potash, we are applying our specific chemical knowledge to the problem of soil replenishment. Besides water and humus, soil is most likely to lack nitrogen, phosphorus, and potash, and in less degreee sulphur and calcium. These then may be specifically added in forms that are convenient, to supplement the original content of the soil, or to make good the losses through crop removal or waste in other ways.

The name potash, strictly speaking potassium oxide, K_2O, means practically any form of potassium compounds in which that metal is available for plants. The famous Stassfurt deposits of Germany, containing vast amounts of potassium chloride and sulphate have supplied the world so completely that other sources of potash have fallen into the background. But wood ashes and the residues from the sugar refineries are fully appreciated and used for their potash value. When the war shut off the European supplies, sources of potash were sought in this country, with partial success.

It has been claimed that phosphorus is that one of the plant foods which is most likely to be lack-

ing in soils, and it must therefore be most often supplied from outside sources. The form in which phosphorus is required is that of the fully oxidized form, the salt phosphate, in a somewhat soluble form. As a mineral source of phosphorus, the rock phosphate deposits $Ca_3(PO_4)_2$, of some of our Southern States, yield an abundant supply. But it is so insoluble that it is advantageous to treat it with sulphuric acid before applying it. By this reaction,

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$

the insoluble rock is converted into two other substances, each of some solubility and of fertilizer value. Another source of phosphorus is the basic slag from furnaces used in the making of steel from iron containing phosphorus. Ores of iron formerly not available for steel making have become especially valuable, because of the perfection of the methods for removing the phosphorus from the iron and absorbing it in the furnace lining.

Nitrogen is the most interesting of this group of specifically required elements. Its great abundance in the free state in the atmosphere, the difficulty of converting it into compounds, and the readiness with which it leaves its compound are features peculiar to nitrogen. Plants require nitrogen to be in the form of fully oxidized nitrates, but most compounds of nitrogen when mixed with the soil readily pass over into nitrates under the influence of bacteria. The problem is therefore not one of nitrates, but simply of any nitrogen compound. The nitrogen cycle already mentioned again comes in for discussion. The interests of agriculture are that nitrogen should never leave this cycle and become free nitrogen. In the use of explosives, nitrogen of necessity is

liberated as the free element and is thus in a manner lost. But otherwise any such conversion of nitrogen compounds to the free elements must be considered a waste. A part may be difficult to avoid, as in the decay of organic matter and the cultivation of the soil, but the wanton waste in the neglect of manures and the burning of garbage should be avoided. In order, then, to keep up the nitrogen content of the soil, or to increase it for more intensive cultivation, we must combine nitrogen with other elements, and thus place it within the chemical charm of the cycle.

THE NITROGEN QUESTION

The natural means of fixing nitrogen are confined on the whole to two. Under atmospheric conditions, electric storms, and perhaps other natural phenomena, small amounts of nitrogen are combined with oxygen or hydrogen, and these compounds finds their way into the soil. Secondly, certain leguminous plants, by means of the nodules formed upon their roots, induced by certain bacteria, are capable of utilizing the atmospheric nitrogen.

The artificial methods of fixing nitrogen have been discussed in another place. Under the stimulus of the need of nitrogen compounds for explosives during the war, great progress has been made in the question of fixation. There will undoubtedly be a diminution in this interest as necessity is less pressing, but what has been so far learned will be available in any future crisis.

THE LIMING OF LANDS

In the decay of organic matter and the formation of humus there is likely to be established an acid

condition of the soil, in which some plants thrive, but which is unfavorable for the good growth of many others. This phase of agricultural chemistry will be better understood in the future. But one feature is already clear, namely, that some crops must have this acid neutralized. The natural antidote for the acid condition established, or its preventative as the acid gradually forms, is lime. That is, calcium hydroxide for quick action, and calcium carbonate, finely ground, for slower action. This action is independent of the requirement of calcium in the normal growth of crops.

This brief sketch of the main features of agricultural chemistry may be summarized as follows: Plants store up energy and food for animals, that is, for men. Their energy is gathered from the sunlight and is dissipated by animals. The materials of plants are taken from the air and soil, and in great part are returned to these reservoirs when the animals have used them. The chief portion of plant structures is built up from carbon dioxide and water, and the minor, but nevertheless essential, portion is taken from the soil in the form of nitrogen and minerals.

Soils are disintegrating rock containing plant foods in forms of varying availability. These are in part mineral, and in part organic, the so-called humus. On account of the cropping of soils these plant foods are gradually exhausted and must be renewed by returning to the soil what has originally come from it, or by supplying some new source of plant food. These represent the natural and the artificial fertilizers. The question of water is most important, but concerns physical and not chemical considerations.

CHAPTER XXIX

THE CHEMISTRY OF NUTRITION

THE chemistry of living matter and its products and processes is included mainly within the scope of organic chemistry. We may call this biochemistry, or, if we are interested in certain phases of it only, chemistry of nutrition. It is almost a self-evident necessity that the chemical nature of tissue and of the foods needed to build it up must be the same. In order to make some beginning of the consideration of these substances, we will make a classification, applicable, with slight reconsideration, to both organisms and their foods. The classes thus distinguished are six — carbohydrates, fats, proteins, simpler organic compounds, water, and mineral matter. The human body is made up of about 60 per cent water, 18 per cent protein, 16 per cent fat, 6 per cent mineral matter, while the carbohydrate present is only about 0.1 per cent. Plants vary considerably in their composition, and it is difficult to make an exact statement which is at the same time brief. But some idea may be obtained from the following rough averages. The nutritious parts of plants average about 24 per cent water, 10 per cent protein, 5 per cent or more of fat, and 60 per cent carbohydrate. In the nonnutritious parts of a plant the water may run as high as 90 per cent, and most of the rest is likely to be carbohydrate in the form of cellulose. A usable

estimate of the amount of mineral matter in plants is about 1 to 2 per cent. The remaining class of substances mentioned, the simpler organic compounds, like alcohols, acids, flavors, and essential oils, are present in such irregular ways that no general statement may be made for them. They will be mentioned as the occasion arises.

It is apparent that protein and fat are predominant in the human, that is, the animal body, while carbohydrates, particularly cellulose and starch, predominate in vegetables. For our present purpose, a convenient distinction between animals and vegetables lies in the manner in which each obtains its food, including both functions of foods, namely the supply of material and the supply of energy. The animal must have its food ready in a highly organized form, such as is found in other animals or plants; the digestive process consists in assimilating these, so far as the material is concerned, and in burning them up, to utilize the energy stored up within them. Plants, on the other hand, use simple inorganic matter for their food, and build it up into complex forms, storing up in them the energy gathered from the sunlight. The animal is dependent upon the plant, and the latter makes use of the waste products of animal life, carbon dioxide, CO_2, water, H_2O, and certain nitrogen compounds. When the plant is through with its process, we have the complicated carbohydrates, fats, and proteins, ready again for the animal's consumption. We thus again meet with the cycles of carbon and nitrogen in nature, in which these elements go the rounds of the three kingdoms of nature, mineral to plant to animal, then back to mineral.

THE CARBON AND HYDROGEN CYCLE.

Carbon dioxide and water
(CO_2 and H_2O)
Plant products are made part of the animal organism, then fully oxidized to carbon dioxide and water.
are built up into plant carbohydrates, fats, and proteins, by plants, and become food for animals.

The energy changes involved in the life of plants and animals, however, do not form a cycle. The original source of our energy is the sunlight. The plant gathers this and stores it away in its compounds. The animal burns up these compounds and thus utilizes this energy. But now this energy is lost by being dissipated as heat to the surroundings. Materials are used over and over again. But the movement of energy is in only one direction; when it is used up it must be replenished from the original source, the sunlight.

CARBOHYDRATES, FATS, AND PROTEINS

The chemistry of the carbohydrates has been fully presented and needs little further mention here. Glycogen, a polysaccharide similar to starch, sometimes called animal starch, assumes a conspicuous place in the process of food absorption. The fats, too, have been touched on sufficiently. However, mention should be made of a number of solids, strongly resembling the fats, yet of different composition. Along with the fats they are classed under the name of lipins, meaning fatlike substances. Such substances are the higher fatty acids, palmitic and stearic, $C_{15}H_{31}CO_2H$ and $C_{17}H_{35}CO_2H$; the sterols, which are higher alcohols, $C_{27}H_{43}OH$; the waxes, similar to fats, but containing an alcohol other than glycerine for a base, $C_{39}H_{61}$ $(OCO.C_{15}H_{31})$,

and certain fats complicated with phosphoric acid, called phospholipins. These all function to some extent as do the fats, and we may assume that they offer more possibilities for the complications useful for living processes.

The chemical composition of the proteins is briefly this: They are made up of various combinations of different amino acids, held together by the group NH. The total molecule is apparently very large, the individual groups being repeated until the total number is perhaps in the neighborhood of one hundred, and the total molecular weight about 15,000. There are external signs of this large molecule, in that the proteins are colloidal, that is, they do not crystallize or diffuse readily, and their solutions foam on shaking. When acted on chemically they break down, and before simple substances are obtained a long series of intermediate compounds can be identified, of which some are apparently of greater importance than others. Tryptophane is so essential that its absence in corn results in the disease called pellagra, when corn proteins alone are used in the diet.

We may summarize. Proteins are complex nitrogen derivatives, more conspicuous in the animal than in the plant, of an average composition: carbon 52 per cent, hydrogen 7 per cent, nitrogen 16 per cent, oxygen 23 per cent, sulphur 2 per cent. Some also contain iron, phosphorus, or iodine. They are solids, odorless and tasteless and almost white. Their solubility with respect to water, alcohol, and salt solutions is variable. Most of them are amorphous (not crystalline) and colloidal. They occur only exceptionally without foreign admixture, and in the animal at least only in the living cell, not in reserve

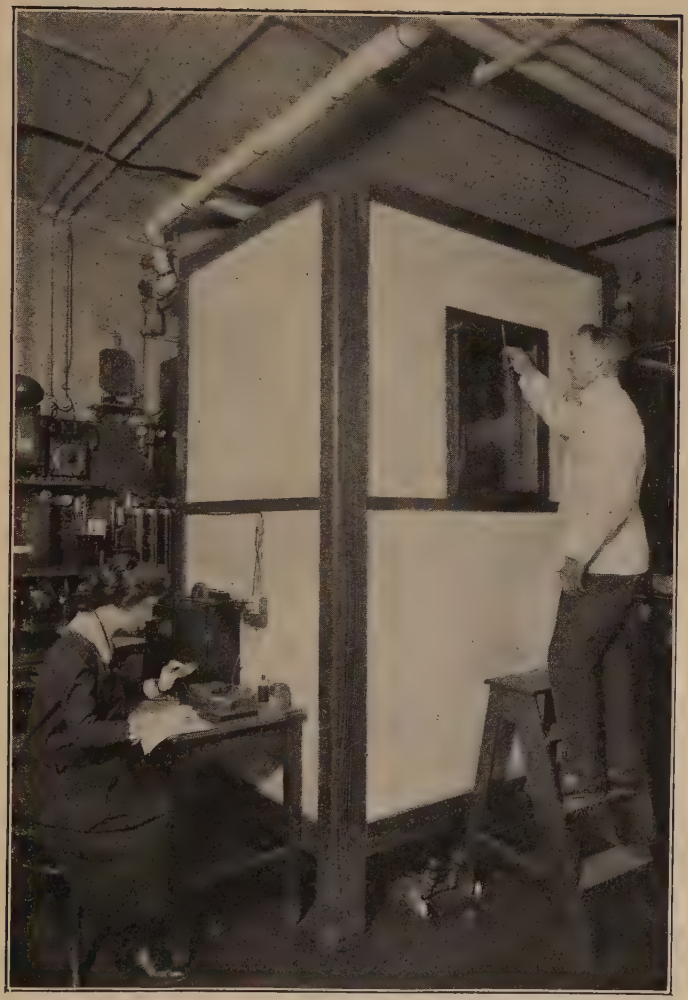
stores. Their most characteristic property is that of coagulation, familiar in the hardening of the white of egg and the curdling of milk. There is usually more than one variety of amino acid present in any given molecule. They are amphoteric, that is, act either on bases or acids, which is to be expected, as they contain both the acid and basic groups of the amino acids. In the process of digestion and absorption they are readily disintegrated and resynthesized.

The theoretically possible number of proteins is a fabulous one, and the actual number known is very large. Out of all the mass of known proteins, the following classification will bring some simplification:

Class 1. The simple proteins, namely, proteins which, no matter how complex the molecule, contain no other constituent besides the amino acids. The variation among them must be due to different combinations of the amino acids. So far as food value goes they are not equal, for some seem to lack certain amino acids apparently necessary for proper building of tissue.

Class 2. These are called the conjugated proteins, because in addition to a composition similar to that of group 1, they have other groups of altogether different nature superadded. They include very vital substances, such as the hemoglobin (red corpuscles) of the blood, and the material of the nucleus of the cell. The variety and complexity of these seem to be the features making them of special value in the more vital parts of the organism.

Class 3. These proteins are called the derived or modified proteins. Proteins are readily altered, probably in the direction of simplification, by the action of heat, water, acids, alkalies, and enzymes



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CALORIMETER, USED IN THE DEPARTMENT OF AGRICULTURE FOR MEASURING HEAT GIVEN OFF BY RIPENING FRUITS

Copyright, Ewing Galloway

LABORATORY ON DAIRY EXPERIMENTAL FARM, DEPARTMENT OF AGRICULTURE

(similar to ferments). The range of intermediate products, before the constituent amino acids are reached, is considerable.

Among the modified proteins may be mentioned especially the polypeptides, artificially prepared by synthesis of amino acids, or obtained from the natural proteins by disintegration. In them the living processes and the laboratory processes meet and they have in consequence a unique interest. Every such point of contact teaches us more about the vital processes and confirms our belief that they are simply specialized forms of ordinary chemical and physical phenomena, and in no wise associated with any incomprehensible vital force.

The fourth group of substances included in organisms and their foods, after carbohydrates, fats, and proteins, may be designated as the simpler organic compounds. When these do not contain nitrogen they present no new features. They are simply the alcohols, aldehydes, acids, and other familiar compounds of organic chemistry. But if they do contain nitrogen they have a more particular relation to the animal body. It is likely that they are formed from the proteins, by processes either normal or abnormal. The most important is urea $CO(NH_2)_2$. It is the compound by which the bulk of the nitrogen is excreted from the system. The elimination of the other common elements, hydrogen, oxygen, and carbon, is very simple. The first two are readily disposed of as water. Carbon leaves the body as carbon dioxide, which is active enough and soluble enough to be capable of absorption, yet not so much so but that it may be thrown off in the lungs. The nitrogen problem is less simple. As an element it is inactive and insoluble, and its simple hydrogen

and oxygen compounds are corrosive. In urea the great activity of ammonia is toned down by the carbonic acid, and the result is a compound of a neutral nature. Urea has a structure represented by the formula $CO.(NH_2)_2$. It is carbonic acid $CO.(OH)_2$ with the two hydroxyl groups replaced by $—NH_2$. It is excreted in the urine, and its amount is considerable, about 30 grams, or one ounce, per day. It undoubtedly has other functions.

A small portion of the nitrogen never reaches the form of urea, but becomes part of compounds of the type of uric acid, $C_5H_4N_4O_3$. To some extent these may be considered normal. Beyond that they give rise to complications from an excess of uric acid in the blood and urine.

MINERAL MATTER

This expression is used to designate the portions of any animal or vegetable substance which do not pass off as gases when the substance is burned. This ash approximately, though not exactly, represents the forms in which the original elements are found in the foods and tissues. There are found the non-metals, sulphur, phosphorus, chlorine, fluorine, and silicon, and the metals, sodium, potassium, calcium, magnesium, and iron, and occasionally one or two other elements. The function of mineral matter is varied. It supplies hard material for building up skeletons (calcium phosphate) and protective coverings as shells (calcium carbonate). Salts in the blood and digestive juices influence their solvent power and their diffusibility while the action of acids and bases is self-evident. Some metals seem to have special functions, perhaps as catalysts, as iron in the blood. Phosphorus is helpful in building

up a variety of molecules, which through a greater complexity serve as the seats of vital processes. It is significant that sea water, with its abundance of mineral matter, is so favorable to the thriving of living things. Small as the amount of mineral in plants and animals is, its rôle is always of definite importance. It is excreted and must be renewed constantly, thus indicating its intimate relation to the changes taking place in the living tissue.

WATER AND THE ANIMAL BODY

In the study of inorganic chemistry the peculiar relation of water to many important reactions is repeatedly noticed. The relation of water to acids and bases, and the ionization of salts in water are good illustrations. This fundamental importance of water in ways both physical and chemical is repeated in the chemistry of the body. Water exhibits certain physical properties to an unusual degree. It has high capillarity, high heat capacity, both as liquid and on changing to vapor, and is a good nonconductor of electricity. Water acts physically by its warming and cooling action, and by its serving as a carrier to disseminate matter through the various parts of the body. It fills the tissue spaces and makes them firm and rigid. Chemically it serves as the medium for the reactions between active substances and can in no way be of less service than it is in the laboratory. The hydrolytic action of water, that is, its power to split carbohydrates, fats, and proteins into their simple constituents, is one of its chief functions. But still another relation of water comes to the front in this matter, namely the relation of water to the colloidal condition. Colloidal solutions represent the

phases of matter related to water intermediate between true solutions and complete lack of any relation. It includes fine suspensions or sediments, jellies and emulsions, as when oil is thoroughly beaten up with water and yoke of eggs. In this colloidal state, as in jellies or emulsions, we have an ideal condition for living tissue, namely, a combination of the solid condition for rigidity, and the liquid condition for chemical reactivity. If a gelatine solution containing salts is allowed to set, it will illustrate this, for it will be rigid, yet will permit chemical reactions to take place. A crude picture of protoplasms may be suggested by the following: Water containing salts in solution is emulsified, that is, churned up, with the desired solids, the proteins, fats, and carbohydrates. Such a mixture, if we can imagine it to be according to some orderly principles, might serve from its physical and chemical characteristics as a proper seat of the chemical reactions of living things.

DIGESTION, ABSORPTION, AND UTILIZATION OF FOOD

The proteins, fats, and carbohydrates which constitute the main portion of our foods are to a great extent insoluble. Even soluble dextrin and cane sugar have molecules so large that they are not directly capable of absorption. The purpose of the digestive process is then to so simplify these complex, insoluble or nondiffusible compounds that they may become absorbable. Water, salts, the simple sugars, and a few other substances need no preliminary simplification. But these form a comparatively small fraction of the whole. The digestive tract, consisting of stomach, small intestine, and large intestine, is adapted to the storing of the

food, converting it chemically into the soluble and diffusible alteration products and finally absorbing it into the body proper.

The three nutrients owe their physical and chemical properties to a great extent to the fact that they are complexes of simpler units. The proteins are made up of many amino-acids, starch of monosaccharide units, and fats of glycerine and the higher organic acids. In each case simplification may take place by the assumption of water.

The changes in all cases are of a similar kind and may be accomplished in the laboratory by the influence of various reagents. In the digestive processes the reagent is the digestive juice belonging to the respective portions of the digestive tract. The active influence in each case is the enzyme suited to the particular need. These enzymes may be considered catalyzers, for they do not seem to be a part of the final products, and a small amount influences a very large amount of material. Enzymes are likely to be confused with ferments, as their action is so similar, but ferments are living organisms, that is, bacteria, while enzymes are chemical substances secreted by various organs of the body. They are easily decomposed by heat, for example, because they are of such complex nature. The action of enzymes in digestion is hydrolytic, that is, splitting by action of water, as shown above, and they are usually classified and named according to the compound upon which they react. Those hydrolyzing starch are called amylases; proteases act on proteins, and lipases on fats. Invertases change double sugars (disaccharides) into monosaccharides. Specific names are given for particular enzymes, as maltase for that one acting on maltose.

The three chief digestive juices are the saliva, the gastric juice of the stomach, and the pancreatic juice introduced into the digestive tract just before the food reaches the small intestine. The total amount of these juices is about five quarts; they are mostly water, the solid content being at the most only a few per cent. The active agent is always an enzyme, suited to the work which it must do. The saliva is practically neutral, the gastric juice acid, and the pancreatic juice alkaline. Each enzyme is effective only in its proper medium.

The final effect of all these juices containing the various enzymes is that the complex nutrients are simplified so that they diffuse readily through the intestinal wall and are received by the circulatory system of the blood and lymph. Yet the units of the nutrients are still present and are capable of resynthesis into the complex substances which the body needs. Just how the reunion is accomplished is not so clear as the simplification process, but the rebuilding of the complex from the simple is as natural, theoretically, as the reverse. We may summarize then, after this manner: The complex, non-absorbable nutrients are hydrolyzed by the digestive juices, being thus converted into simple diffusible units. These units then pass through the intestinal wall and are resynthesized for the uses of the body or burned for heat and energy.

Absorption of the digested foods begins in the stomach, but is more rapid in the small intestine, which, with its large surface exposure, is well constructed for this purpose. Absorption is completed in the large intestine, and the unabsorbed residue, which is not large, is excreted. After passing the intestinal wall, the absorbed monosaccharides pass

into the blood, are carried to the liver, there resynthesized into glycogen and temporarily stored as such. This glycogen is reconverted into glucose and passed on to the tissue as needed. The fats, partly finely divided, but mainly in the form of fatty acids, pass into the lymph (the fluid supplementary to and emptying into the blood) are reformed into fats and stored or used as needed. The protein fragments pass into the blood and presently are built up again to serve the particular needs of the body.

THE UTILIZATION OF THE DIFFERENT NUTRIENTS

Proteins are needed to build up new tissue and to replace old tissue, for there is a considerable wastage inherent in the mere process of living. In the end, after it has served its main purpose, protein is burned up and supplies heat and energy. As protein is the most difficult nutrient to procure, and also involves the most complex methods of excretion, the use of protein as food beyond its special requirement is disadvantageous.

The fats, after they are reformed, are carried by the blood to the different tissues, where they are either oxidized at once or stored for future use. Some may be incidentally converted into glucose, but its ultimate utilization is the same.

The carbohydrates are utilized to some extent directly by the oxidation of the monosaccharides. Some may be stored temporarily as glycogen, either in the liver or the muscles, but apparently never for a long time. For more permanent storing, the carbohydrates are converted into fat, for the ultimate aim of both is the same, the supplying of the body with heat and energy.

FUEL VALUE AND FOOD REQUIREMENTS

In the study of chemical reactions, the development of heat is such a striking feature that we soon come to look upon it as a sign of the intensity of chemical affinities. Measurements of the amount of heat liberated offer valuable information. In the

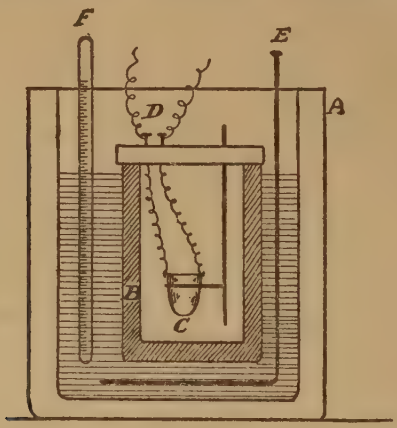


DIAGRAM OF THE BOMB CALORIMETER

A is a case designed to prevent the passage of any heat to or from its contents. It contains water in which is immersed the strong bomb B. The sample is placed in C, and the chamber is filled with compressed oxygen. When all is ready, the sample is fired by the current introduced at D. The heat of the combustion is communicated to the water surrounding B (which is stirred by E), and the change of temperature is recorded by the thermometer F.

case of fuels this is of course particularly true, and in the case of purchases on a large scale the heat value of coals is carefully determined. This is done by means of the calorimeter, a tight chamber in which the sample under consideration is burned in an atmosphere of oxygen. This chamber is immersed in an outer cylinder filled with water, and

all the heat of the action is absorbed by the water. Knowing the amount of the water and the elevation of its temperature, the calculation of the amount of heat is simple. It is measured in calories, namely the amount of heat needed to raise the temperature of a unit weight of water one degree.

All this applies to foods, for they are used in part for the amount of energy which they may develop upon being burned. When measured in such a calorimeter it is found that one gram of fat yields 9,300 calories, that is, heat enough to raise the temperature of 9,300 grams of water 1° C. One gram of protein yields 5,700 calories and 1 gram carbohydrate 4,100 calories. This variation is due to the fact that they are already oxidized in varying degrees. When the nutrients are burned in the body, it would be a fair presumption that the amount of heat liberated would be the same as in the calorimeter.

For the purpose of testing this point the respiration calorimeter has been devised, in which a man could be inclosed and measurements of matter and heat carefully made. The results confirm the presumption and we now know that the fuel value is the same when developed in a calorimeter or in the body.

To this statement the proteins offer an apparent exception, as they are not completely burned up but leave the body as urea. For this reason 1,600 calories are lost, and the body fuel value of proteins is only 4,100 calories. These numbers being inconveniently large, the major calorie, 1,000 times as large, is ordinarily used as the unit, so that our fuel values are, respectively, 9.3 Cal., 4.1 Cal., and 4.1 Cal.

FOOD REQUIREMENTS

The ordinary food requirements are six: proteins, carbohydrates, fats, water, mineral matter and the condiments, like the flavors, organic acids, and similar substances. To the list of these six the vitamines should be added as a seventh, although we know little more about them than that they are essential. All these classes of food necessities are of course supplied to us by our daily menu. A brief analysis of our foods will reveal the fact that they are very similar, differing only in the proportions in which they include the same nutrients, and in the condiments which accompany them. Further, a survey of all our foods will show that the list of these is a comparatively short one, comprehended under the following few classes: (1) meats, including (2) fish; (3) fats, including oils; (4) milk and milk products; (5) eggs; (6) cereals; (7) bread; (8) starch and sugar; (9) fruits; (10) vegetables; (11) potatoes; (12) nuts; (13) condimental substances.

1. Meats. A convenient impression of the composition of meat, free from bone, is that it is made up of water 60 per cent, protein 20 per cent, and fat 20 per cent. Individual cuts may vary considerably. Meat further contains salts and meat extractives, which add flavor and in the latter case have a certain stimulating value. The latter feature applies to broths made from meats, but the tissue-building proteins do not go into solution. Beef extracts are good only for flavor and mild stimulation.

2. Fish serve practically the same purpose as meat, namely to supply protein and to a lesser extent fat. The protein content is about the same

as that of meat, but the fat averages only 6 per cent. From a practical standpoint the waste, almost one-half, is important.

3. Fats and oils. Usually we assume no essential advantages in the use of one fat or oil over another (barring butter fat). Usage and convenience seem to be determining factors, and within comparatively few years there has been a distinct revolution in feeling in this matter. Substitutes for the more expensive butter fat and olive oil are no longer scorned.

4. Milk. It will be impossible to condense into a few lines all the points of chemical interest in connection with milk. The composition of ordinary rich milk is about 3 per cent protein, 4 per cent fat, and 5 per cent milk sugar. The mineral matter is under 1 per cent. In many communities the legal requirement of 3 per cent butter fat is not much exceeded, and the total solids often run below 12 per cent. Although the fat of milk is usually looked upon as its most desirable constituent, the great value of the protein must not be overlooked, and this applies especially to skim milk. Milk, valuable as it is, is a perfect food only for the young of the animal from which the milk is obtained. For the feeding of infants modification is needed. The addition of water diminishes the proportion of protein, while the fat and sugar content are increased by the addition of cream and milk sugar. Cheese includes the protein and fat of milk. Its composition varies considerably, for we know all kinds, from that made of skim milk to that containing much cream. Ordinarily full cheese may contain about 30 per cent of both protein and fat. The value of this as food is evident.

Butter usually contains about 15 per cent water. The most striking feature of butter fat is that there is present in it about 6 per cent of acids low in the fatty acid series. These may be separated readily and determined. As no other fat contains any considerable amount, this forms the readiest way to distinguish between butter and a butter substitute.

5. Eggs contain about 13 per cent protein and 10 per cent fat. Eggs are said to supply 3 per cent of the total food of the country.

6. The cereals, barley, buckwheat, corn, oats, rice, rye, and wheat. The cereals, in the form called air dry, contain about 10 per cent of water. Their protein content averages 11 per cent, fat 2 per cent, and carbohydrate makes up most of the rest. In some of the milled products the more valuable constituents run even higher. Cereals are valuable foods, available as they are at low cost, even if the nutrients are not so fully utilized in the process of digestion as are those of the animal foods.

7. Bread. Wheat has a reasonably high protein content, and on account of the gluten developed in the flour the consistency of the dough is such as to make good bread. It is par excellence the cereal which men prefer. As made up in bread, the food contains 30 per cent of water. The evident lack of fat is made good by the use of butter and other fats. Wheat is an excellent starting point for the simple attainment of a properly balanced ration, a lesson we learned in the provisioning of our armies abroad.

8. Sugar and starch. The great popularity of sugar in the menu is of comparatively recent development, and a proper one, for as an attractive and economical food sugar stands high. It is the

purest food which we can buy. It is true that it has some peculiar disadvantages. Its good flavor may induce overuse, and on account of its solubility digestive disturbances may be caused by its fermentation. Starch is very pure, but its practical advantages over the cereals are not sufficiently pronounced to give it a peculiar place in the popular esteem.

9. Fruits. Fruits are made up so largely of water that it would not be far from the mark to say that they are used mainly for their flavor. The water content varies from 77 per cent in grapes to over 90 per cent in watermelons. The solid part is mostly carbohydrates and the nutritious part of this is sugar. Used in such large amounts as grapes and apples are, their sugar content may be of moment in fulfilling the daily requirement for carbohydrates. Fruits are valuable in the general stimulation of the activities of the digestive tract. Bananas are almost in a class by themselves, being as solid as potatoes. A food article which thus combines flavor with substance is a valuable asset to the menu.

10. Vegetables. These should be divided into two classes. Those resembling cucumbers and tomatoes, which are mostly water, and those like shelled beans, peas, and corn, which are comparatively solid. The first class is comparable with fruit, possessing high condimental value, while the second class has in addition a high food value. The latter, when dried, are in a class with the cereals.

11. Potatoes are only about one-fifth solid, mostly starch. Hence they should be available at low cost to compare with the cereals. They have become very essential in the menu, apparently, and seem to be purchased regardless of price.

12. Nuts are high in fats and proteins and have food value comparable with that of meat.

13. Condiments. Protein, starch, and fat have no pronounced taste and the variety of flavor in foods depends largely upon other substances of little food value, present in small amounts. Sugar is a marked exception to this statement, as it is unique in combining flavor with food value. The food value of the vegetable acids present in foods, as well as that of spices and flavors, is practically negligible. The essential matter of spices ordinarily present is minute. The extracts and the salts of meats must be considered as condiments. When these have been removed from meat, the latter is unpalatable, but is said to be well digested nevertheless. Alcoholic beverages, of the so-called "light" class, have condimental value, and are much used in European countries to round out a rather meager fare. It is clear that alcohol is burned in the system, that is, it is a true food. The objections to its use lie in other directions.

Many studies have been made of the amount of the three nutrients consumed in the ration of people free to choose. These dietary studies have been made with groups of people as well as of selected groups, and finally confirmed in studies by means of the respiration calorimeter. From all these studies it is clear that men select their food in such a way that there is an average daily ration of protein, and of fuel-furnishing foods, fat and carbohydrates supplementing each other. The conclusions drawn may be stated thus: In America the daily dietary for a man exerting himself moderately is protein, 100 grams, or 3.6 ounces; fat, a like amount; carbohydrate, 400 grams, or 14.6 ounces. This has a total

heat value of 3,000 calories. For absolute rest the ration is less, and for very hard work it exceeds this by more than 50 per cent. Women and children require less, but studies of growing boys have shown an almost startling consumption of food.

Experiments with the respiration calorimeter make it possible to work out the disposal of this food, both as to the material and energy involved. It was learned that life processes consume no energy, but that all the potential energy of the food appears as heat, passes off in the excreta, or is used up in evaporating the water from the body. When the subject of the experiment performs work, he requires more food, but only 20 per cent of the energy of this added food appears in the work done, the rest appearing as heat. That is, the efficiency of the human machine, with respect to the added food is 20 per cent, while the efficiency with respect to the total food is only 15 per cent. This compares with the efficiency of a good steam engine. Such experiments as have been performed to study the energy consumed by brain work have had negative results.

THE CHEMISTRY OF COOKING

Cooking has not developed greatly as a science. It is in the stage of an art, in which there has been much accumulated experience without a full understanding of the causes underlying the results obtained. The chemical points involved in cooking are few, and are touched on in the following brief outline.

Cooking sterilizes food. The modern tendency is to obviate the need of this by proper preparation and inspection, but under certain conditions it is a necessary precaution. Heat accomplishes some chemical

changes also. In the case of meat the blood is coagulated so that the meat is no longer red, the fiber is softened by the conversion of the tough connective tissue into tender gelatine. The fiber contracts due to loss of water, albumens coagulate to form crusts, and there are undefinable changes in the proteins and fats which result in their acquiring an attractive flavor. When meats are boiled, salts and extractives pass out from the meat to the broth. It is probably true that cooked meat is less digestible than the uncooked meat, but the difference is slight. Eggs are coagulated by heat, but the disadvantage of hard-boiled eggs is due perhaps only to lesser mastication. Milk is evidently altered by boiling, and this feature is watched carefully where a diet needs attention.

The cooking of vegetables is more important than that of meats. The swelling and breaking of the starch grains, the rupturing of the cellulose walls, the softening of gelatinous substances, all serve to render the food more adaptable to the action of the digestive juices. Pleasant flavors may be developed and sometimes an unpleasant flavor is removed. Bread making is one of the most complex operations of cooking. It involves the leavening of the loaf either by the development of fermentation or the use of baking powders, both involving chemical changes which can be studied in detail. Other changes are not so clear. The proteins coagulate to some extent and make combinations with the starch. The starch on the surface of the loaf is altered, forming dextrin, which, colored by substances on the order of caramel (formed by overheating sugar and starch), help to form the crust. The final result is a combination of crust and crumb which appeals

to the appetite and which is readily permeated by the digestive juices.

The selection of food is as important, perhaps, as the actual manipulation in the cooking processes. Selection involves the proper proportion between animal and vegetable sources, the attainment of a balanced ration, the consideration of digestibility, and the best use of condiments. Proper comminution, consistency, volume, and temperature are hardly chemical points, but in a full discussion of the matter they must be given a place. In the final result, it is only too apparent that in the present state of our knowledge experience is of greater moment than scientific knowledge. The latter is only slowly making progress in solving the many questions which arise within the field.

THE VITAMINES

In the consideration of the foods necessary to proper nutrition, the vitamines have in recent years been found to play a vital part. It is now an old story that the disease called beriberi is caused by the lack of some substance present in the hulls of rice. When these hulls were removed the food became incapable of supporting life. There are then most important substances present in our foods in such small amounts that we can observe them only indirectly. These are the vitamines. Our knowledge of them is only beginning. Vitamines seem to be organic, nitrogen compounds, but not proteins. There are both water soluble and fat soluble forms, and the former is less likely to be lacking than the latter. Fat soluble vitamines are present in butter fat, eggs, and many other natural foods, and absent from vegetable fats and oils. Without vitamines

there can be no proper growth or maintenance of health. Although the vitamines are only of recent discovery, we have been familiar in the past with the special value of some foods for reasons which could not then be explained. The incident of the loss when rice was polished warns us that in the artificial manipulation of foods the possible effect on vitamines must not be overlooked.

FOOD ADULTERATION

Adulterations take on two main forms: one is the introduction for one reason or another of some harmful substance; the other is the substitution of some harmless yet less desirable constituent for one of greater value. Misbranding is an offense of the latter order.

The national pure food law covers the adulteration and misbranding of both foods and drugs. The essential features of the law are as follows: The drug article must conform to the name by which it goes, when the meaning of that name is well established; it must conform to the statements on its own label, and the label must bear no device which gives a misleading impression. Certain drugs may not be present without a statement of the amounts, and the weight in the package must be indicated. With respect to foods, they may contain nothing to reduce or injuriously affect quality or strength, there may be no substitute, no extraction of a valuable constituent, no addition of deleterious or poisonous matter, no spoiled matter or product from an animal not killed by slaughter. Confectionery, interpreted somewhat broadly, is in a class by itself. The essence of this matter is that as long as there is nothing harmful present the article will pass.

As the purpose is to please the eye or the palate, no restrictions except those of safety need be applied.

FOOD PRESERVING

Men of a grade of civilization past the hunting stage, and living in a temperate climate, must make provision for a winter food supply, while the congestion of our population in great cities introduces the question of food preserving into all seasons. The first solution of the problem is through the selection of the grains, which with their low water content are stable for an indefinite time. Other foodstuffs, as potatoes, may be kept with care for a reasonable period. Fats and oils are very stable. But a conscious act of preserving is necessary for many foods.

Drying comes into the first consideration. Enormous amounts of food are dried, as fruits, fish, and meats. Dried cattle food is in the end for men. During the exigencies of the war the question of desiccating food for the purpose of solving transportation difficulties has raised a very vital question as to whether this manner of handling foods should not be extended into new fields. So far the progress has been slight, but there is always hope for the future. Cold storage is so well known that it needs only to be mentioned. Sterilization by heat is likely to be confined in the household to the easier operations, such as the preserving of fruits and some vegetables. The more difficult operations, as the canning of meats, require the more complete resources of the factory. There is a possibility of progress, through the more thorough study of household problems which the future will certainly bring. The result may be the extension of house-

hold practice; or it may be the relegation to the factory of the few household industries still extant. Associated with sterilization is the use of such substances as sugar, salt, spices, vinegar. Smoking is not very remote from these. The efficiency of these methods is due perhaps to the establishing of a general environment unfriendly to bacterial life.

These methods of preserving are all in high favor. The desirability of chemical preservatives is at least open to discussion. The common inorganic preservatives used are sulphur dioxide and sulphites of sodium and calcium, potassium nitrate, boric acid (also called boracic acid) and borax, as also fluorides. Among organic substances benzoic acid or its sodium salt is perhaps the most used. Salicylic acid is common and formaldehyde is effective. The use of some of these is legalized and has many defenders. The whole subject of chemical preservatives has caused much discussion, and some experiments have been made, but no final agreement has yet been reached. The objections raised to their use are as follows: They are substances not suitable for taking into the system and are therefore definitely harmful; they give a false appearance of freshness; they prevent the development of signs with which we are familiar, which we ordinarily rely on as a warning that the food is spoiling; they permit carelessness in preparation. Until the matter has been so thoroughly investigated that all doubt is removed, it would seem wise to assume on the whole a conservative attitude. As the presence of all such preservatives must be declared on the labels, no consumer is compelled to accept them.

GLOSSARY

Acid.—A compound made up of a nonmetallic group and of hydrogen, so constituted that this hydrogen is replaceable by metals with the formation of salts. It is neutralized by a base, with the formation of a salt and water. When dissolved in water it yields positive hydrogen ions and negative nonmetallic ions.

Adsorption.—The retention on the part of a solid by surface attraction of gases or liquids, as the adsorption of gases by charcoal.

Alcohol.—A general name for compounds of the paraffin series formed by the introduction of one or more hydroxyl groups in place of hydrogen. Ordinary alcohol is the best known example.

Aldehyde.—Any compound containing the group —C(=O)—H. This group is very reactive, and especially sensitive to oxygen.

Aliphatic.—A general name applied to the paraffin series of hydrocarbons and their derivatives.

Alkali.—An active basic compound, usually the hydroxide, of the metals of the sodium group. The term is applied also to the metals of this group and to their compounds in a general way.

Allotropic Forms.—The various forms of the same element, as oxygen and ozone, diamond and charcoal, differing by a varied number or arrangement in the molecule of atoms of the same kind.

Amalgam.—An alloy, one of the constituent metals of which is mercury.

Amide.—A compound obtained by replacing the hydroxy group of an organic acid by means of the amino group, as acetamide.

Amine.—A compound derived from ammonia by the replacement of its hydrogen by certain radicals.

Amino.—A prefix applied to the names of certain compounds containing the group —NH_2, as amino-acid.

Amorphous.—Without crystalline form.

Anhydride.—An oxide of a nonmetal (or of an organic acid group) capable of uniting with water to form an acid. Sulphuric anhydride with water forms sulphuric acid.

Aromatic.—A general name applied to the hydrocarbons of the benzene series, and their derivatives.

Ash.—The noncombustible and nonvolatile residue from the burning of animal or vegetable matter representing approximately the original mineral content. It may be an essential constituent, as the ash of milk, or an admixture, as the salt of butter.

-ate.—A suffix applied to the names of salts of the oxy-acids characterized by the suffix *-ic.* Nitric acid forms nitrates.

Atoms.—The smallest particle, portion or proportion of matter which enters into chemical reactions or compounds. It is the unit of chemical relations.

Base.—The hydroxide of a metal capable of uniting with an acid. The name is also applied to hydroxides of organic radicals, and in a broad way is applied to the positive metallic or nonacid portion of a salt.

Benzene.—The name of the fundamental member of the second hydrocarbon series of organic chemistry. The term is applied as an adjective to designate a relationship to this series.

Bond.—The conventional assumption of the unit of linkage between atoms and radicals. The hydrogen atom is used as the basis for estimating its value, and it is conveniently represented by a dash, —, but this must not be interpreted as a material or rigid connection.

Calorie.—The unit of heat, being the amount needed to heat one unit weight of water one degree. The gram and centigrade degree give a convenient unit for small quantities of heat, and 1,000 times this amount for larger quantities. A calorie can also be computed in the English system of weights and measures.

Carbohydrate.—An organic compound composed of carbon, hydrogen, and oxygen, the last two in the proportions of

water, as $C_6H_{12}O_6$. They are all composed of similar simple combinations called monosaccharides, or of unions of two or more of these simple combinations. The various forms of sugars, starch, and cellulose make up this carbohydrate group.

Carboxyl.—The acid group, $-C\overset{\overset{\displaystyle O}{\|}}{-}OH$ of organic acids.

Catalyzer. — A substance which accelerates or retards a chemical action without entering into the final products.

Chain.—A term applied to a number of carbon atoms linked together, forming the main portion of an organic compound of the paraffin series.

Colloidal.—The relation between two substances in which one holds the other in a dispersed state evenly disseminated throughout its mass, but not in the form of solution. Jellies and emulsions offer good illustrations.

Compound.—A substance formed by the definite chemical union of two or more elements. In the union the elements lose their individuality and the compound possesses its own characteristic properties.

Determination.—The measurement in any expedient manner of the amount of a particular constituent of a compound or mixture.

Disaccharide.—One of the sugar groups, containing two of the simple sugar units. Ordinary cane sugar, milk sugar, and maltose are the most common.

Dissociate.—To separate into parts in such a manner that these parts may reunite under changed conditions to re-form the original compound.

Double Decomposition.—The reaction between a salt and an acid, base, or other salt, involving the simple interchange of the positive groups (metal or hydrogen) and the formation of a new pair of compounds. Illustration: sodium chloride and silver nitrate yield silver chloride and sodium nitrate.

Electrolysis. — (Decomposition by electricity.) Acids, bases and salts in aqueous solution conduct electricity, and when a current is passed, the positive constituent is liberated at the negative pole, and the negative constituent at the positive pole. This process may also be carried out on fused bases and salts.

Electrolyte.—Any substance (as acids, bases, and salts) is capable of conducting electricity. The name suggests both conductivity and electrolysis.

Electromotive Series.—The list of the metals placed in the order of their reactivity in certain respects; it gives an approximate idea of the general nature of the metals.

Element.—A substance which is incapable of being resolved by any known means into simpler parts. It is the basis of the compounds.

Enzyme.—A complex chemical compound, secreted by various plant and animal organisms, capable of catalytically bringing about certain changes which are more frequently hydrolytic than otherwise.

Equation.—An expression borrowed from algebra, used to indicate the nature of a reaction and the proportions of the reacting substances.

Ester.—An organic salt, made up of an organic base and any acid, more usually an organic acid. Ethyl acetate.

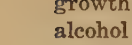
Ether.—A compound formed by the linking together of two alcohol radicals by means of oxygen. $C_2H_5—O—C_2H_5$. The oxygen marks also the place of separation of the two groups. Complex sugars have a somewhat similar structure.

Ethyl.—C_2H_5, the second and most important radical of the paraffin series of hydrocarbons. C_2H_5Cl, ethyl chloride.

Fat.—A mixture of esters made up of the organic base, glycerine, and three fatty acid groups. Glyceryl stearate. The liquid fats, or oils, are also included under this term.

Ferment.—A living organism, bacterium, which by its growth brings about chemical changes, as the production of alcohol from sugar.

Formula.—The group of symbols used to indicate the composition and structure of a compound. The symbols are sometimes so arranged that they show the exact relation of the atoms in the molecule. The formula is then called graphic, or structural. Formula, HNO_3. Structural formula



-gen.—A suffix indicating producing or generating. Hydrogen = producing water.

Glucose.—$C_6H_{12}O_6$, also called dextrose, grape or starch sugar, is the most important simple sugar or monosaccharide, and is the constituent or one of the constituents of the more common complex carbohydrates.

Group.—(*a*) Same as *Radical.* (*b*) A number of substances which are considered together on account of their similarity.

Halogen.—A general name given to the elements of the chlorine group, fluorine, chlorine, bromine, and iodine, indicating the readiness with which they form salts with the metals. (Greek, hal = Latin, sal, salt.)

Halogenation.—Introduction of a halogen.

Hardness.—(*a*) The comparative readiness with which a solid may be scratched. This is determined by reference to an arbitrary scale numbered 1 to 10. Hardness and specific gravity are not related. Lead is heavy but soft, glass is light but hard.

(*b*) The soap-destroying power of water, caused by the presence usually of calcium and magnesium salts.

Hydro-acid.—An acid of the type, hydrochloric acid, HCl, containing no oxygen.

Hydrogenation.—The addition of hydrogen to organic compounds, especially the fatty oils, which contain less than the normal amount of hydrogen.

Hydrolysis.—(Decomposition by water.) The resolution of a compound made up of two or more individualized groups, into these groups, by the addition of water. The linkage between the groups is broken, one group uniting with hydrogen, the other with hydroxyl of water. Hydrolysis applies only to substances which may be assumed to be formed by the union of these groups by the loss of water.

Hydroxide.—A basic compound, containing the hydroxyl group, —OH. The terms base and hydroxide are in many cases synonymous.

Hydroxyl.—The group —OH, derived from water, present in many compounds, which contain both hydrogen and oxygen, as bases and acids.

-ic.—A suffix applied, (*a*) To the name of most important oxy-acid derived from any given nonmetal. The suffix *-ous* indicates an acid with less oxygen.

(*b*) When an element combines with another element or group in more than one proportion, the suffix *-ic* is applied to the name of the first element to indicate the compound containing the greater proportion of the second element or group, as *-ous* is used to indicate the smaller proportion. CuCl, $CuCl_2$, cuprous and cupric chlorides.

-ide.—The suffix applied to the name of the second constituent of a compound indicates that it contains only two elements; it is applied also to compounds made up of groups which are considered as single units, as ammonium chloride, $(NH_4)Cl$.

Indicator.—A substance which by color changes shows the progress of a chemical reaction.

Inorganic.—Pertaining to any chemical discussion involving compounds which are not organic; from the standpoint of the natural sciences associated with the mineral kingdom.

Ion.—A group, carrying one or more positive or negative electric charges, derived from acids, bases, or salts dissolved in water. Ions are either positive hydrogen or metallic, or negative hydroxyl or nonmetallic.

Ionization.—The dissociation of an ionogen into its constituent ions upon solution in water.

Ionogen.—A convenient term applied to acids, bases, and salts, because upon solution in water they yield ions. Ionogen and electrolyte ordinarily denote the same substances.

Isomerism.—The condition exhibited by different compounds which are composed of the same elements in the same proportions as C_2H_2 and C_6H_6. The more interesting phases of isomerism involve identical similarity in the absolute number of atoms, and a similarity in nature of the compounds, but a distinction due to a different arrangement of the atoms in the molecule, as ethylene and ethylidene chlorides, $CH_3.CHCl_2$ and $CH_2Cl.CH_2Cl$.

-ite.—The suffix applied to the names of salts derived from acids designated by the suffix *-ous*. Sulphurous acid yields sodium sulphite.

Kinetic.—Pertaining to the motion of molecules.

Latent Heat.—(latent = concealed.) The molecular or kinetic energy of the liquid or gaseous state, appearing in the form of sensible heat when the physical state is changed

to one of lower molecular energy, gas to liquid, liquid to solid. An equal amount of sensible heat must be applied in order to bring about the reverse changes.

Metal.—An element capable of replacing directly or indirectly the hydrogen of an acid, of forming a base, and of forming by itself a positive ion. The popular idea of a metal includes more than half of these elements, but the metals of the sodium and potassium group must be included to make the list complete.

Methyl.—CH_3—; the first radical of the paraffin series of hydrocarbons, CH_3Cl, methyl chloride.

Mineral.—(*a*) An element or compound as found in a natural state. Rocks may contain several minerals, but each mineral is a definite chemical substance.

(*b*) The term applied to the constituents of animal or vegetable matter aside from carbon, hydrogen, oxygen, and nitrogen. They are present in the ash of such substances.

Molar Solutions.—The solution obtained by dissolving the gram-molecular weight of any substance, usually in water, so as to make a total of one liter of solution. The molar solution of calcium hydroxide contains 74 grams. $Ca(OH)_2$, $40+2\times16+2\times1=74$.

Molecule.—The smallest units of which any substance is composed. These units are composed of several kinds of atoms, as the molecules of water, H_2O, of one kind of atom, as oxygen, O_2, and in some cases, as argon, of single atoms. The molecule is the physical unit, as the atom is the chemical unit.

Monosaccharide.—See *Carbohydrate.*

Nitro.—(*a*) The name applied to the group —NO_2, derived from nitric acid by the elimination of its hydroxyl group.

(*b*) A prefix applied to organic compounds containing this group, as nitrobenzene, $C_6H_5NO_2$.

Nonmetal.—An element possessing characteristics in a sense the opposite of those of a metal. Nonmetals combined with hydrogen alone, or with hydrogen and oxygen, form acids, and are included in the negative ions. They lack the usual external characteristics associated with metals.

Normal Solutions.—Molar solutions so modified that they represent one valence or combining weight. The molar solu-

tion and normal solution of hydrochloric acid, HCl, are the same, but in the cases of sulphuric acid, H_2SO_4, and phosphoric acid, H_3PO_4, the molar solution must be diluted to one-half and one-third concentration, respectively, in order to convert it into normal solution.

Organic.—Pertaining to compounds included under the head, hydrocarbons and their derivatives. The name is derived from the fact that in the early years of chemistry, the compounds included in this study were assumed to be of necessity products of organized life. Although such a limitation is incorrect, products of animal and vegetable life are very important in organic chemistry.

Oxidation.—Primarily the process of adding oxygen to any substance; it has however been applied more broadly to increasing the valence of certain elements and even to subtracting hydrogen.

Oxide.—The compound of an element with oxygen. The oxides of metals and of nonmetals are of very different character.

Oxy-acid.—Inorganic acids containing oxygen, as sulphuric acid. They may be assumed to be made up by the union of nonmetallic oxides with water.

Paraffin. — The name of the first series of the hydrocarbons; the name indicates that these hydrocarbons possess a low affinity for acids. Also called the methane, marsh gas, aliphatic or fatty acid series.

Per.—A prefix indicating a higher degree of valence than the usual. In lead oxide, PbO, the valence of lead is 2, in lead peroxide, PbO_2, its valence is 4.

Phenol.—A general name for hydroxyl derivatives of the benzene hydrocarbons, corresponding to some extent to the alcohols of the paraffins.

Precipitate.—The act or product of forming an insoluble solid from ingredients which were soluble. The formation and nature of precipitates formed under known conditions are so characteristic that they are the readiest means of detecting unknown substances.

Protein.—Complex nitrogen compounds common in animal tissue. Egg white and horn are typical.

Radical.—A group of elements, as ethyl, C_2H_5, or sulphate,

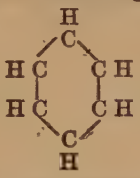
SO_4, preserving its unity through various reactions. Often called group or residue.

Reaction.—The action between two chemical substances. Also a change caused in one under influence of physical force. It is so frequently represented by equations that the terms are easily confused.

Reagent.—Any active chemical substance; more exactly one applied for the accomplishment of some specific purpose.

Reduction.—The opposite of oxidation in its various meanings.

Residue.—The same as group or radical.

Ring.—A combination of carbon (or other) atoms in which, besides the linking of adjacent atoms, those somewhat remote are linked together, thus forming a ring. The benzene ring  is the most important example.

Saccharide.—See *carbohydrate, di-* and *poly-saccharide.*

Salt.—The product obtained by replacing the hydrogen of an acid by means of a metal; by the mutual action of a base and acid; by the union direct or indirect of positive metallic and negative nonmetallic groups. The statements represent the same facts from somewhat different aspects.

Saponification.—(Soap making.) The decomposition of an ester, especially a fat, by the action of a strong base. This base unites with the acid, and the base of the ester, the alcohol, is set free.

Series.—A group of similar substances, which differ in such a way in respect to composition and properties that they exhibit a regular progression. The series of organic compounds are conspicuous examples.

Specific Gravity.—The ratio of the weight of solids and liquids to that of equal volumes of water. The corresponding constant for a gas is conveniently expressed by stating the weight of one liter of the gas under standard conditions. This value, multiplied by 22.4, the gram-molecular volume, gives the molecular weight of the gas.

Specific Heat.—The ratio of the heat capacity of a substance to that of water.

Solute.—The substance dissolved in a solvent.

State, Physical State.—The solid, liquid, or gaseous condition.

Unsaturated.—(*a*) Physical, as of a solution, capable of taking up more of a given substance.

(*b*) Chemical, the condition of hydrocarbons or hydrocarbon residues containing less than their normal content of hydrogen.

Valence.—The combining value of any element or group, compared with that of hydrogen, which is taken as unity. Each such unit considered as one linkage and may be represented by a bond. Valence 1, H—Cl, valence 2, Ca=O, valences 1 and 2, $^{H}\!\!>\!\!O$. 8 is the highest valence known. The valence of any element or group may usually be recognized by inspection of the formula of its hydrogen or oxygen compound.

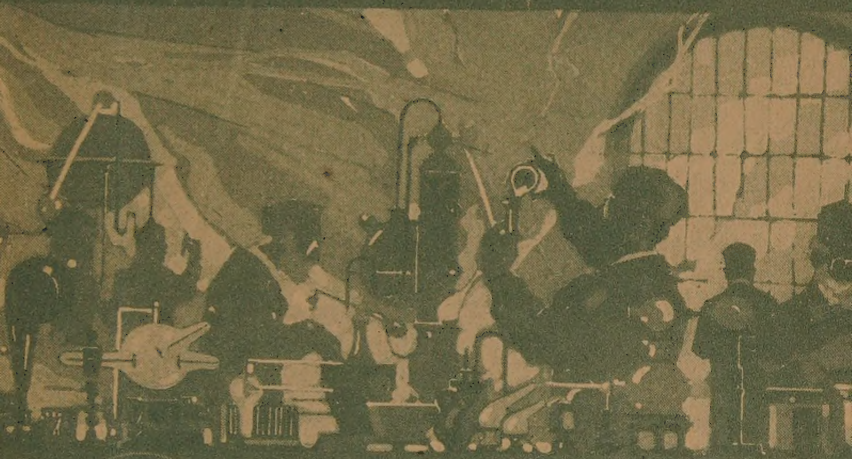
TABLE OF ELEMENTS

International Atomic Weights, 1922

Elements	Symbols	Atomic Weights	Elements	Symbols	Atomic Weights
Aluminium	Al	27.0	Molybdenum	Mo	96.0
Antimony	Sb	120.2	Neodymium	Nd	144.3
Argon	A	39.9	Neon	Ne	20.2
Arsenic	As	74.96	Nickel	Ni	58.68
Barium	Ba	137.37	Niton	Nt	222.4
Bismuth	Bi	209.0	Nitrogen	N	14.008
Boron	B	10.9	Osmium	Os	190.9
Bromine	Br	79.92	Oxygen	O	16.0
Cadmium	Cd	112.40	Palladium	Pd	106.7
Cæsium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorine	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Rubidium	Rb	85.45
Columbium	Cb	93.1	Ruthenium	Ru	101.7
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	45.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.1
Fluorine	F	19.0	Silver	Ag	107.88
Gadolinium	Gd	157.3	Sodium	Na	23.0
Gallium	Ga	70.1	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.0	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.15
Indium	In	114.8	Thulium	Tm	169.9
Iodine	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium	Yb	173.5
Lutecium	Lu	175.0	Yttrium	Y	89.33
Magnesium	Mg	24.32	Zinc	Zn	65.37
Manganese	Mn	54.93	Zirconium	Zr	90.6
Mercury	Hg	200.6			

COMPARISON OF CENTIGRADE AND FAHRENHEIT TEMPERATURE SCALES

Centigrade	Fahrenheit	Centigrade	Fahrenheit
—150°	—238°	50°	122°
—100	—148	60	140
—30	—22	70	158
—20	—4	80	176
—10	+14	90	194
—5	+23	100	212
0	+32	150	302
5	+41	200	392
10	50	250	482
20	68	300	572
30	86	350	662
40	104	400	752

The Metals in the Order of Their Specific Gravity	
Lithium	0.53
Potassium	0.87
Sodium	0.98
Calcium	1.6
Magnesium	1.7
Strontium	2.5
Aluminium	2.7
Barium	3.8
Arsenic	5.7
Chromium	6.7
Antimony	6.6
Zinc	7.1
Tin	7.3
Manganese	7.4
Iron	7.9
Cobalt	8.6
Copper	8.9
Bismuth	9.8
Silver	10.5
Lead	11.3
Mercury	13.6
Gold	19.3
Platinum	21.5

The Metals in the Order of Their Fusibility		
Mercury	—39°C.	—38°F.
Potassium	63	145
Sodium	98	208
Tin	232	449
Bismuth	265	510
Lead	326	620
Zinc	419	786
Antimony	630	1166
Magnesium	630	1166
Aluminium	655	1210
Calcium	800	1472
Silver	960	1760
Gold	1060	1940
Copper	1080	1976
Manganese	1250	2282
Nickel	1450	2640
Iron	1500	2730
Platinum	1750	3180